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[Name of Document] Specification 1  
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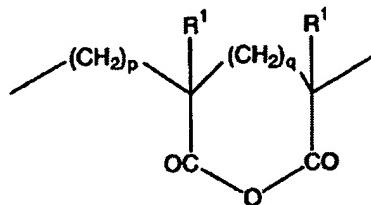
[Name of Document] SPECIFICATION

[Title of the Invention] SEAL PRODUCT

[Claims]

[Claim 1] A seal product produced by molding an acrylic block copolymer (A) comprising a methacrylic polymer block (a) and an acrylic polymer block (b), at least one of the polymer blocks containing, in its main chain, an acid anhydride group (c) represented by formula (1) and (or) a group derived from the acid anhydride group:

[Chem. 1]



(wherein R<sup>1</sup>'s each represent a hydrogen atom or a methyl group and may be the same or different, p represents an integer of 0 or 1, and q represents an integer of 0 to 3).

[Claim 2] The seal product according to claim 1, wherein the acrylic block copolymer (A) contains 10% by weight to 60% by weight of the methacrylic polymer block (a) and 90% by weight to 40% by weight of the acrylic polymer block (b).

[Claim 3] The seal product according to claim 2, wherein the acrylic block copolymer (A) contains 0.1% by weight to 50% by weight of a unit having a carboxyl group (d).

[Claim 4] The seal product according to claim 1, 2, or 3,

wherein the acrylic polymer block (b) includes 50% by weight to 100% by weight of at least one of butyl acrylate, ethyl acrylate, and 2-methoxyethyl acrylate, and 0% by weight to 50% by weight of another acrylate and (or) vinyl monomer copolymerizable with the acrylate.

[Claim 5] The seal product according to claim 1, 2, 3, or 4, wherein the acrylic block copolymer (A) is produced by atom transfer radical polymerization.

[Claim 6] A seal product comprising a rubber-containing composition containing 0.5% by weight to 90% by weight of the acrylic block copolymer (A) according to claim 1, 2, 3, 4, or 5, and 99.5% by weight to 10% by weight of crosslinked and (or) uncrosslinked rubber (B).

[Claim 7] A seal product comprising a rubber-containing composition prepared by dynamically heat-treating 0.5% by weight to 90% by weight of the acrylic block copolymer (A) according to claim 1, 2, 3, 4, or 5, and 99.5% by weight to 10% by weight of uncrosslinked rubber (B1).

[Claim 8] A seal product comprising a composition containing 0.5% by weight to 90% by weight of the acrylic block copolymer (A) according to claim 1, 2, 3, 4, or 5, and 99.5% by weight to 10% by weight of a thermoplastic resin (C) and (or) a thermoplastic elastomer (D).

[Claim 9] The seal product according to claim 8, comprising a composition prepared by dynamically heat-

treating the acrylic block copolymer (A) according to claim 1, 2, 3, 4, or 5, and the thermoplastic resin (C) and (or) the thermoplastic elastomer (D).

[Claim 10] The seal product according to claim 1, 2, 3, 4, 5, 6, 7, 8, or 9, comprising 0.1 parts by weight to 30 parts by weight of a lubricant (E) and (or) 0.1 parts by weight to 100 parts by weight of an inorganic filler (F) on the basis of 100 parts by weight of the acrylic block copolymer (A).

[Claim 11] The seal product according to claim 6, 7, 8, 9, or 10, wherein the acrylic block copolymer (A) contains a 2-methoxyethyl acrylate unit.

[Claim 12] The seal product according to claim 6, 7, 8, 9, or 10, wherein the acrylic block copolymer (A) contains a 2-methoxyethyl acrylate unit, a butyl acrylate unit, and an ethyl acrylate unit.

[Claim 13] The seal product according to claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12, wherein the seal product is used for an automobile, household electric appliance, or office electric appliance.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to seal products for automobiles, home electric appliances, or office electric appliances, all of which are produced using nonconventional acrylic block copolymers or compositions comprising the acrylic block copolymers rich in flexibility and excellent in oil resistance, moldability, mechanical physical properties, and compression set, and further rich in reactivity.

[0002]

[Description of the Related Art]

The types of seal products for automobiles, seal products for home electric appliances, and seal products for office electric appliances are roughly divided into rotating seals, reciprocating seals, and isolated seals. Specific examples of the seals include an oil seal, a lip packing, a dust cover, and the like.

[0003]

Examples of materials used for these seals include nitrile rubber (NBR), acrylic rubber (ACM), silicone rubber (VMQ), and chloroprene rubber (CR). However, these rubber materials are mainly vulcanized (crosslinked) for generally improving physical properties, such as low compressive strain and oil resistance.

[0004]

Vulcanized rubber generally has excellent flexibility

and excellent rubber elasticity, but has the problem of moldability. For example, in injection molding, it is necessary that rubber is mixed with an additive, and the resultant mixture is kneaded and then supplied into a mold, followed by vulcanization. Therefore, injection molding requires a special molding machine, a long molding cycle time, and a complicated process.

[0005]

Also, extrusion molding has the same problem and thus has a problem in mass-production of vulcanized rubber products.

[0006]

Furthermore, vulcanized rubber is disadvantageous in that it is not melted even by reheating after molding and vulcanization, and thus it cannot be post-processed by bonding or the like.

[0007]

In view of the above-described situation, in recent years, thermoplastic elastomers have been increasingly used in place of vulcanized rubber. Among various thermoplastic elastomers, olefinic thermoplastic elastomers have been used in increasing amounts from the viewpoints of lightweight, environmental pollution resistance, and economics. Various seal parts such as a glass run channel, a weather strip, and the like are used for automobiles. Although most of these

parts are formed using vulcanized rubber, some of the seal parts have recently been formed using lightweight, recyclable olefinic thermoplastic elastomer compositions from the viewpoint of improvement in fuel consumption and environmental problems. For example, there has been proposed a thermoplastic elastomer composition prepared by dynamically heat-treating, in the presence of a crosslinking agent, a mixture containing ethylene- $\alpha$ -olefin-unconjugated polyene copolymer rubber (A) at a molar ratio (ethylene/ $\alpha$ -olefin) of ethylene of 55/45 to 70/30 to an  $\alpha$ -olefin having 3 to 20 carbon atoms, and an olefin resin (B) at a specified ratio (refer to, for example, Patent Document 1).

[0008]

[Patent Document 1]

Japanese Unexamined Patent Application Publication No.  
2001-316487 (pp. 3 - 7)

[0009]

[Problems to be Solved by the Invention]

However, olefinic thermoplastic elastomers have insufficient weather resistance, oil resistance, and ozone resistance in comparison to vulcanized rubber. Therefore, the thermoplastic elastomers have difficulty in use for parts required to have the above-described requirements, and development of thermoplastic elastomers satisfying the requirements has been demanded.

[0010]

An object of the present invention is to develop seal products, such as seal products for automobiles, seal products for home electric appliances, and seal products for office electric appliances, each of which is formed using an acrylic block copolymer rich in flexibility and excellent in oil resistance, moldability, mechanical physical properties, and compression set, and also rich in reactivity.

[0011]

[Means for Solving the Problems]

As a result of studies for solving the above-described problems, it was found that a seal product produced by molding an acrylic block copolymer comprising a methacrylic polymer block (a) and an acrylic polymer block (b), at least one of the polymer blocks containing a specified acid anhydride group in its main chain, is rich in flexibility and excellent in oil resistance, moldability, mechanical physical properties, and compression set, and is further rich in reactivity. This finding resulted in the completion of the present invention.

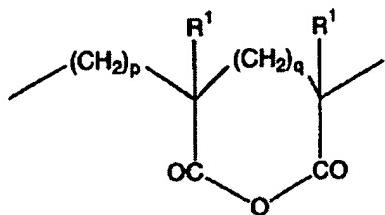
[0012]

Namely, the present invention relates to a seal product produced by molding an acrylic block copolymer (A) comprising a methacrylic polymer block (a) and an acrylic polymer block (b), at least one of the polymer blocks

containing, in its main chain, a unit (c) having an acid anhydride group represented by formula (1) and (or) a group derived from the acid anhydride group:

[0013]

[Chem. 2]



[0014]

(wherein R¹'s each represent a hydrogen atom or a methyl group and may be the same or different, p represents an integer of 0 or 1, and q represents an integer of 0 to 3)  
(claim 1).

The seal product according to claim 1, wherein the acrylic block copolymer (A) contains 10% by weight to 60% by weight of the methacrylic polymer block (a) and 90% by weight to 40% by weight of the acrylic polymer block (b)  
(claim 2).

The seal product according to claim 2, wherein the acrylic block copolymer (A) contains 0.1% by weight to 50% by weight of a unit having a carboxyl group (d) (claim 3).

The seal product according to claim 1, 2, or 3, wherein the acrylic polymer block (b) includes 50% by weight to 100%

by weight of at least one of butyl acrylate, ethyl acrylate, and 2-methoxyethyl acrylate, and 0% by weight to 50% by weight of another acrylate and (or) vinyl monomer copolymerizable with the acrylate (claim 4).

The seal product according to claim 1, 2, 3, or 4, wherein the acrylic block copolymer (A) is produced by atom transfer radical polymerization (claim 5).

A seal product comprising a rubber-containing composition containing 0.5% by weight to 90% by weight of the acrylic block copolymer (A) according to claim 1, 2, 3, 4, or 5, and 99.5% by weight to 10% by weight of crosslinked and (or) uncrosslinked rubber (B) (claim 6).

A seal product comprising a rubber-containing composition prepared by dynamically heat-treating 0.5% by weight to 90% by weight of the acrylic block copolymer (A) according to claim 1, 2, 3, 4, or 5, and 99.5% by weight to 10% by weight of uncrosslinked rubber (B1) (claim 7).

A seal product comprising a composition containing 0.5% by weight to 90% by weight of the acrylic block copolymer (A) according to claim 1, 2, 3, 4, or 5, and 99.5% by weight to 10% by weight of a thermoplastic resin (C) and (or) a thermoplastic elastomer (D) (claim 8).

The seal product according to claim 8, comprising a composition prepared by dynamically heat-treating the acrylic block copolymer (A) according to claim 1, 2, 3, 4,

or 5, and the thermoplastic resin (C) and (or) the thermoplastic elastomer (D) (claim 9).

The seal product according to claim 1, 2, 3, 4, 5, 6, 7, 8, or 9, comprising 0.1 parts by weight to 30 parts by weight of a lubricant (E) and (or) 0.1 parts by weight to 100 parts by weight of an inorganic filler (F) on the basis of 100 parts by weight of the acrylic block copolymer (A) (claim 10).

The seal product according to claim 6, 7, 8, 9, or 10, wherein the acrylic block copolymer (A) contains a 2-methoxyethyl acrylate unit (claim 11).

The seal product according to claim 6, 7, 8, 9, or 10, wherein the acrylic block copolymer (A) contains a 2-methoxyethyl acrylate unit, a butyl acrylate unit, and an ethyl acrylate unit (claim 12).

The seal product according to claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12, wherein the seal product is used for an automobile, household electric appliance, or office electric appliance (claim 13).

[0015]

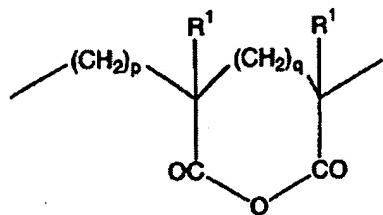
[Description of the Embodiments]

A seal product of the present invention is produced by molding an acrylic block copolymer (A) including a methacrylic polymer block (a) and an acrylic polymer block (b), at least one of the polymer blocks containing, in its

main chain, a unit having an acid anhydride group (c) represented by formula (1) and (or) a group derived from the acid anhydride group (c):

[0016]

[Chem. 3]



[0017]

(wherein R¹'s each represent a hydrogen atom or a methyl group and may be the same or different, p represents an integer of 0 or 1, and q represents an integer of 0 to 3). The acrylic block copolymer (A) preferably includes 10% by weight to 60% by weight of the methacrylic polymer block (a) and 90% by weight to 40% by weight of the acrylic polymer block (b).

[0018]

The seal product of the present invention will be described in detail below.

[0019]

<Acrylic block copolymer (A)>

The acrylic block copolymer (A) may have the structure of a linear block copolymer or a branched (star) block

copolymer, or a mixture thereof. The structures of the acrylic block copolymer (A) are properly used according to the physical properties of the acrylic block copolymer (A) required for various seal products and the required processing properties and mechanical properties of a composition with rubber (B) and a thermoplastic resin (C) which are possibly used for improving the low-temperature brittleness of the acrylic block copolymer (A). However, in view of cost and polymerizability, a linear block copolymer is preferred.

[0020]

The structure of the linear block copolymer is not particularly limited. From the viewpoint of the physical properties of the linear block copolymer or the physical properties of a composition, the acrylic block copolymer is preferably at least one block copolymer selected from the group consisting of block copolymers represented by formulae  $(a-b)_n$ ,  $b-(ab)_n$ , and  $(a-b)_n-a$  ( $n$  is an integer of 1 or more, e.g., an integer of 1 to 3) wherein the methacrylic polymer block (a) (referred to as the "polymer block (a)" or the "block (a)" hereinafter) is denoted by a, and the acrylic polymer block (b) (referred to as the "polymer block (b)" or the "block (b)" hereinafter) is denoted by b. Among these types, an  $(a-b)$ -diblock copolymer, an  $(a-b-a)$ -triblock copolymer, or a mixture thereof is preferred from the

viewpoint of handleability in processing seal products, and the physical properties of compositions.

[0021]

Furthermore, at least one unit (c) having an acid anhydride group (simply referred to as the "acid anhydride group-containing unit (c)" hereinafter) represented by formula (1) may be contained in at least one of the polymer blocks. When two or more units are introduced, polymerization of a monomer containing the unit may be random copolymerization or block copolymerization.

[0022]

With respect to the type of copolymerization of the acid anhydride group-containing unit (c), for example, in the type of an (a-b-a)-triblock copolymer, the structure can be (a/c)-b-a, (a/c)-b-(a/c), c-a-b-a, c-a-b-a-c, a-(b/c)-a, a-b-c-a, and a-c-b-a. In these expressions, (a/c) means that the block (a) contains the acid anhydride group-containing unit (c), and (b/c) means that the block (b) contains the acid anhydride group-containing unit (c). The expressions of c-a- and a-c- mean that the acid anhydride group-containing unit (c) is bonded to an end of the block (a). All the expressions (a/c), (b/c), c-a-, and a-c- belong to the block (a) or (b).

[0023]

The number-average molecular weight of the acrylic

block copolymer (A) may be determined according to the required molecular weights of the methacrylic polymer block (a) and the acrylic polymer block (b). When the molecular weight is small, the block copolymer (A) may exhibit insufficient mechanical properties as an elastomer, while when the molecular weight is excessively large, processing characteristics may deteriorate. From this viewpoint, the number-average molecular weight of the acrylic block copolymer (A) is preferably 30,000 to 500,000, more preferably 40,000 to 400,000, and most preferably 50,000 to 300,000.

[0024]

The ratio ( $M_w/M_n$ ) of the weight-average molecular weight ( $M_w$ ) to the number-average molecular weight ( $M_n$ ) of the acrylic block copolymer (A) according to gel permeation chromatographic measurement is preferably 1 to 2, and more preferably 1 to 1.8. With the ratio ( $M_w/M_n$ ) over 2, the uniformity of the acrylic block copolymer (A) may deteriorate.

[0025]

The composition ratios of the methacrylic polymer block (a) and the acrylic polymer block (b) which constitute the acrylic block copolymer (A) may be determined according to the physical properties required for a seal product, the moldability required for processing compositions, and the

required molecular weights of the methacrylic polymer block (a) and the acrylic polymer block (b). For example, the composition ratio of the methacrylic polymer block (a) preferably ranges from 5% by weight to 80% by weight, more preferably 10% by weight to 70% by weight, and most preferably 10% by weight to 60% by weight. The composition ratio of the acrylic polymer block (b) preferably ranges from 95% by weight to 20% by weight, more preferably 90% by weight to 30% by weight, and more preferably 90% by weight to 40% by weight. When the ratio of the methacrylic polymer block (a) is less than 5% by weight, rubber elasticity at high temperatures tends to decrease, while when the ratio exceeds 80% by weight, the mechanical properties of elastomers, particularly breaking elongation, tends to decrease, or the flexibility tends to decrease.

[0026]

Assuming that the glass transition temperatures of the methacrylic polymer block (a) and the acrylic polymer block (b) which constitute the acrylic block copolymer (A) are  $Tg_a$  and  $Tg_b$ , respectively, the glass transition temperatures of the methacrylic polymer block (a) and the acrylic polymer block (b) preferably satisfies the following relationship:

$$Tg_a > Tg_b$$

[0027]

The glass transition temperature ( $Tg$ ) of each of the

polymer blocks (the methacrylic polymer block (a) and the acrylic polymer block (b)) can be determined using the weight ratio of the monomer of each polymer block according to the following Fox's equation.

$$1/Tg = (W_1/Tg_1) + (W_2/Tg_2) + \dots + (W_m/Tg_m)$$

$$W_1 + W_2 + \dots + W_m = 1$$

(wherein Tg represents the glass transition temperature of a polymer block, Tg<sub>1</sub>, Tg<sub>2</sub>, ..., Tg<sub>m</sub> each represent the glass transition temperature of a homopolymer of each monomer, and W<sub>1</sub>, W<sub>2</sub>, ..., W<sub>m</sub> each represent the weight ratio of each monomer.

[0028]

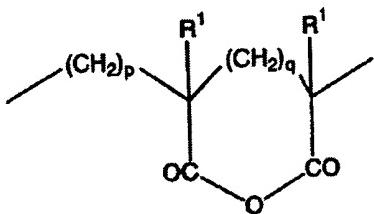
As the glass transition temperature of each homopolymer in the above Fox's equation, for example, the value described in Polymer Handbook Third Edition (Wiley-Interscience 1989) is used in the specification.

[0029]

The acid anhydride group-containing unit (c) represented by formula (1) may be introduced into the acrylic block copolymer by any method without limitation.

[0030]

[Chem. 4]



[0031]

(wherein R¹'s each represent a hydrogen atom or a methyl group and may be the same or different, p represents an integer of 0 or 1, and q represents an integer of 0 to 3). However, from the viewpoint of easy introduction and easy purification after introduction, the acid anhydride group-containing unit (c) is preferably introduced in the form of a functional group, which is a precursor of the acid anhydride group-containing unit (c), into the acrylic block copolymer and then subjected to cyclization.

[0032]

In formula (1), q is an integer of 0 to 3, preferably 0 or 1, and more preferably 1. When q is 3 or more, polymerization tends to be complicated, or cyclization to the acid anhydride group tends to become difficult.

[0033]

In formula (1), p is an integer of 0 or 1. When q is 0, p is preferably 0, and when q is 1 to 3, p is preferably 1. The acid anhydride group-containing unit (c) may be introduced in one or both of the methacrylic polymer block

(a) and the acrylic polymer block (b). The acid anhydride group-containing unit (c) may be introduced according to the reactive site of the acrylic block copolymer (A), cohesive force and glass transition temperatures of the blocks which constitute the acrylic block copolymer (A), and the physical properties of the acrylic block copolymer (A) required for various seal products. For example, when the methacrylic polymer block (a) or the acrylic polymer block (b) is desired to be selectively modified or reacted with a compound having an amino group, a hydroxyl group, or an epoxy group using a six-membered acid anhydride group-containing unit as a reactive site, the acid anhydride group-containing unit (c) may be introduced into a block which is desired to be modified or reacted. In view of improvement in the heat resistance and thermal decomposition resistance of the acrylic block copolymer (A), the acid anhydride group-containing unit (c) may be introduced into the methacrylic polymer block (a). From the viewpoint that rubber elasticity is imparted to the acrylic block copolymer (A), the acid anhydride group-containing unit (c) may be introduced as a cross-linking reactive site (cross-linking point) into the acrylic polymer block (b). From the viewpoint of control of the reactive site, heat resistance, and rubber elasticity, the acid anhydride group-containing unit (c) is preferably introduced into either the

methacrylic polymer block (a) or the acrylic polymer block (b). When the acid anhydride group-containing unit (c) is introduced into the methacrylic polymer block (a), both R<sup>1</sup>s in formula (1) are preferably methyl groups, and when the acid anhydride group-containing unit (c) is introduced into the acrylic polymer block (b), both R<sup>1</sup>s in formula (1) are preferably hydrogen atoms. Where both R<sup>1</sup>s are hydrogen atoms when the acid anhydride group-containing unit (c) is introduced into the methacrylic polymer block (a), and both R<sup>1</sup>s are methyl groups when the acid anhydride group-containing unit (c) is introduced into the acrylic polymer block (b), a polymerization operation for the acrylic block polymer (A) becomes complicated, and a difference between the glass transition temperatures of the methacrylic polymer block (a) and the acrylic polymer block (b) tends to decrease to decrease the rubber elasticity of the acrylic block copolymer (A).

[0034]

A preferred range of contents of the acid anhydride group-containing unit (c) depends on the cohesive force and reactivity of the acid anhydride group-containing unit (c), the structure and composition of the acrylic block copolymer (A), the number of the constituent blocks of the acrylic block copolymer (A), and the glass transition temperature thereof, and the introduction site and form of the acid

anhydride group-containing unit. For example, the content of the acid anhydride group-containing unit (c) is preferably in a range of 0.1% by weight or more and more preferably 0.5% by weight or more, and 99.9% by weight or less, more preferably 80% by weight or less, and particularly preferably 60% by weight or less, relative to the whole of the acrylic block copolymer (A). With the content of less than 0.1% by weight, the reactivity of the acrylic block copolymer (A) and compatibility with thermoplastic resins may become insufficient. When the acid anhydride group-containing unit (c) having high Tg is introduced into the methacrylic polymer block (a) serving as the hard segment in order to improve the heat resistance of the polymer block (a), with the content of less than 0.1% by weight, the heat resistance may not be sufficiently improved to decrease the expression of rubber elasticity at high temperatures. On the other hand, with the content of over 99.9% by weight, cohesive force may excessively increase, thereby degrading workability.

[0035]

The block containing the acid anhydride group-containing unit (c) and the content thereof may be appropriately determined according to the cohesive force and glass transition temperature, reactivity to the crosslinked rubber and/or uncrosslinked rubber (B), the thermoplastic

resin (C) and/or the thermoplastic elastomer (D), and the reactive sites which are required for various seal products.

[0036]

From the viewpoint of further improvement in heat resistance and cohesive force, the acrylic block copolymer (A) may contain a unit (d) having a carboxyl group (referred to as a "carboxyl group-containing unit (d)" hereinafter). For example, the carboxyl group-containing unit (d) can be produced in the process for introducing the acid anhydride group-containing unit (c) into the acrylic block copolymer (A).

[0037]

The carboxyl group-containing unit (d) may be introduced into only one or both of the methacrylic polymer block (a) and the acrylic polymer block (b). In view of the reactive site of the acrylic block copolymer (A), the cohesive force and glass transition temperatures of the constituent blocks of the acrylic block copolymer (A), and the required physical properties of the acrylic block copolymer (A), the carboxyl group-containing unit (d) may be appropriately introduced according to purposes. From the viewpoint of control of the reactive site of the acrylic block copolymer (A) and ease of introduction of the carboxyl group-containing unit (d) into the acrylic block copolymer (A), the carboxyl group-containing unit (d) is preferably

introduced into the block containing the acid anhydride group-containing unit (c). From the viewpoint of heat resistance and cohesive force, the carboxyl group-containing unit (d) is more preferably introduced into the methacrylic polymer block (a). This is because when the carboxyl group-containing unit (d) having high Tg and high cohesive force is introduced into the hard segment, the rubber elasticity can be further expressed even at a high temperature. From the viewpoint of compatibility with crosslinked and (or) uncrosslinked rubber, the thermoplastic resin, and (or) the thermoplastic elastomer, the carboxyl group-containing unit (d) is preferably introduced into the acrylic polymer block (b).

[0038]

The number of the carboxyl group-containing unit (d) per polymer block may be at least one. When the number is 2 or more, polymerization of a monomer containing the carboxyl group-containing unit (d) may be random copolymerization or block copolymerization. For example, in the type of an (a<sub>1</sub>-b<sub>1</sub>-a<sub>1</sub>)-triblock copolymer, the structure can be (a<sub>1/d</sub>)-b<sub>1</sub>-a<sub>1</sub>, (a<sub>1/d</sub>)-b<sub>1</sub>-(a<sub>1/d</sub>), d-a<sub>1</sub>-b<sub>1</sub>-a<sub>1</sub>, d-a<sub>1</sub>-b<sub>1</sub>-a<sub>1</sub>-d, a<sub>1</sub>-(b<sub>1/d</sub>)-a<sub>1</sub>, a<sub>1</sub>-b<sub>1</sub>-d-a<sub>1</sub>, and a<sub>1</sub>-d-b<sub>1</sub>-a<sub>1</sub>.

[0039]

In these expressions, (a<sub>1/d</sub>) means that the block (a<sub>1</sub>) contains the carboxyl group-containing unit (d), and (b<sub>1/d</sub>)

means that the block (b1) contains the carboxyl group-containing unit (d). Since the acid anhydride group-containing unit (d) is also contained, (a1) means the methacrylic polymer block in which the acid anhydride group-containing unit is introduced in a random form or block form, and (b1) means the acrylic polymer block in which the acid anhydride group-containing unit is introduced in a random form or block form. In the block (a1) or (b1), the introduction site and form of the carboxyl group-containing unit (d) may be freely determined according to purposes. All the expressions of (a1/d), (b1/d), d-a1-, and a1-d- belong to the block (a) or (b).

-- [0040]

A preferred range of the content of the carboxyl group-containing unit (d) depends on the cohesive force of the carboxyl group-containing unit (d), the structure and composition of the acrylic block copolymer, the number of the constituent blocks of the acrylic block copolymer, and the introduction segment and form of the carboxyl group-containing unit (d).

[0041]

For example, the content of the carboxyl group-containing unit (d) preferably ranges from 0 to 50% by weight, more preferably 0.1 to 50% by weight, and most preferably 0.5 to 40% by weight, of the constituent monomers

of the acrylic block copolymer (A). When the acrylic block copolymer (A) is required to have higher heat resistance and cohesive force, the carboxyl group-containing unit (d) is preferably introduced within a range to 50% by weight. With the content of over 50% by weight, the carboxyl group-containing unit (d) tends to cyclize with an adjacent ester unit at a high temperature, and thus the physical properties after molding tend to change, thereby causing difficulty in producing products with stable physical properties. When the carboxyl group-containing unit (d) is produced in the process for introducing the acid anhydride group-containing unit (c), 0.1% by weight or more of the carboxyl group-containing unit is generally produced. When less than 0.1% by weight of the carboxyl group-containing unit (d) is introduced into the hard segment, heat resistance and cohesive force may not be sufficiently improved.

[0042]

The content of the carboxyl group-containing unit (d) is represented by percent by weight of a monomer originally containing the carboxyl group-containing unit or a monomer having the carboxyl group-containing unit produced by reaction or the like.

[0043]

Specific examples of the acrylic block copolymer (A) include the acrylic block copolymers produced in Examples 1

to 7 using the acrylic block copolymers produced in Production Examples 1 to 4, the acrylic block copolymer produced in Production Example 6, and the amido group-containing acrylic block copolymer produced in Example 8.

[0044]

<Methacrylic polymer block (a)>

The constituent monomer of the methacrylic polymer block (a) preferably satisfies the relation  $Tg_a > Tg_b$  between the glass transition temperatures of the methacrylic polymer block (a) and the acrylic polymer block (b) which constitute the acrylic block copolymer (A). From the viewpoint of easy production of the acrylic block copolymer (A) having desired physical properties, cost, and availability, the monomer preferably comprises 0% by weight to 90% by weight, preferably 0% by weight to 85% by weight, of a methacrylate, 5% by weight to 100% by weight, preferably 15% by weight to 100% by weight, of a monomer having a functional group which serves as a precursor of the acid anhydride group-containing unit (c) or the carboxyl group-containing unit (d), and 0% by weight to 50% by weight, preferably 0% by weight to 25% by weight, of another vinyl monomer copolymerizable therewith. When the ratio of the methacrylate is excessively low, the characteristics of methacrylates, for example, weather resistance, high glass transition temperatures, and compatibility with resins, tend to

deteriorate. When the ratio of the methacrylate is excessively high, flexibility tends to degrade.

[0045]

The required molecular weight of the methacrylic polymer block (a) may be determined according to the cohesive force of the methacrylic polymer block (a) required for various seal products, and the time required for polymerization therefor.

[0046]

The cohesive force is considered to depend on molecular interaction (i.e., polarity) and a degree of entanglement. As the molecular weight increases, the number of entanglement points increases to increase the cohesive force. Namely, assuming that the required molecular weight of the methacrylic polymer block (a) is  $M_A$ , and the molecular weight between entanglement points of the constituent polymer of the methacrylic polymer block (a) is  $M_{CA}$ , a preferred example of the  $M_A$  range is  $M_A > M_{CA}$  when cohesive force is required, and  $M_A > 20M_{CA}$  when higher cohesive force is required. When a moderate degree of cohesive force and a creeping property are simultaneously satisfied, the  $M_A$  range is preferably  $M_{CA} < M_A < 20M_{CA}$ . As the molecular weight between entanglement points, the value described in the document by Wu, et al. (Polym. Eng. and Sci., 1990, vol. 30, p. 753) may be referred to. For example, on the assumption

that the methacrylic polymer block (a) entirely comprises methyl methacrylate, when the cohesive force is required, a preferred example of the number-average molecular weight of the methacrylic polymer block (a) is in a range of 9200 or more. However, when the acid anhydride group-containing unit (c) is introduced into the methacrylic polymer block (a), the cohesive force is imparted by the acid anhydride group-containing unit (c), and thus the molecular weight can be set to a lower value. Since the polymerization time tends to increase as the number-average molecular weight increases, the number-average molecular weight may be determined according to the required productivity. However, the number-average molecular weight is preferably 200,000 or less, and more preferably 100,000 or less.

[0047]

Examples of the constituent methacrylate of the methacrylic polymer block (a) include methacrylic acid aliphatic hydrocarbon (for example, alkyl having 1 to 18 carbon atoms) esters, such as methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, n-pentyl methacrylate, n-hexyl methacrylate, n-heptyl methacrylate, n-octyl methacrylate, 2-ethylhexyl methacrylate, nonyl methacrylate, decyl methacrylate, dodecyl methacrylate, and stearyl methacrylate; methacrylic acid alicyclic hydrocarbon esters,

such as cyclohexyl methacrylate and isobornyl methacrylate; methacrylic acid aralkyl esters, such as benzyl methacrylate; methacrylic acid aromatic hydrocarbon esters, such as phenyl methacrylate and toluyl methacrylate; methacrylic acid esters with functional group-containing alcohols having ether oxygen, such as 2-methoxyethyl methacrylate and 3-methoxybutyl methacrylate; and methacrylic acid fluoroalkyl esters such as trifluoromethylmethylethyl methacrylate, 2-trifluoromethylethyl methacrylate, 2-perfluoroethylmethylethyl methacrylate, 2-perfluoroethyl-2-perfluorobutylethyl methacrylate, 2-perfluoroethyl methacrylate, perfluoromethyl methacrylate, diperfluoromethylmethylethyl methacrylate, 2-perfluoromethyl-2-perfluoroethylmethylethyl methacrylate, 2-perfluorohexylethyl methacrylate, 2-perfluorodecylethyl methacrylate, and 2-methacrylate, 2-perfluorohexadecylethyl methacrylate. These compounds may be used alone or in combination of two or more. Among these methacrylates, methyl methacrylate is preferred from the viewpoint of compatibility with a thermoplastic resin to be combined, cost, and availability.

[0048]

Examples of the vinyl monomer copolymerizable with the constituent methacrylate of the methacrylic polymer block (a) include acrylates, aromatic alkenyl compounds, vinyl cyanide compounds, conjugated diene compounds, halogen-

containing unsaturated compounds, unsaturated dicarboxylic acid compounds, vinyl ester compounds, and maleimide compounds.

[0049]

Examples of the acrylates include acrylic acid aliphatic hydrocarbon (for example, alkyl having 1 to 18 carbon atoms) esters, such as methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, isobutyl acrylate, n-pentyl acrylate, n-hexyl acrylate, n-heptyl acrylate, n-octyl acrylate, 2-ethylhexyl acrylate, nonyl acrylate, decyl acrylate, dodecyl acrylate, and stearyl acrylate; acrylic acid alicyclic hydrocarbon esters, such as cyclohexyl acrylate and isobornyl acrylate; acrylic acid aromatic hydrocarbon esters, such as phenyl acrylate and toluyl acrylate; acrylic acid aralkyl esters, such as benzyl acrylate; acrylic acid esters with functional group-containing alcohols having ether oxygen, such as 2-methoxyethyl acrylate and 3-methoxybutyl acrylate; and acrylic acid fluoroalkyl esters, such as trifluoromethylmethyl acrylate, 2-trifluoromethylethyl acrylate, 2-perfluoroethylacrylate, 2-perfluoroethyl-2-perfluorobutylethyl acrylate, 2-perfluoroethyl acrylate, perfluoromethyl acrylate, diperfluoromethylmethyl acrylate, 2-perfluoromethyl-2-perfluoroethylmethyl acrylate, 2-perfluorohexylethyl acrylate, 2-perfluorodecylethyl acrylate,

and 2-perfluorohexadecylethyl acrylate.

[0050]

Examples of the aromatic alkenyl compounds include styrene,  $\alpha$ -methylstyrene, p-methylstyrene, and p-methoxystyrene.

[0051]

Examples of the vinyl cyanide compounds include acrylonitrile and methacrylonitrile.

[0052]

Examples of the conjugated diene compounds include butadiene and isoprene.

[0053]

Examples of the halogen-containing unsaturated compounds include vinyl chloride, vinylidene chloride, perfluoroethylene, perfluoropropylene, and vinylidene fluoride.

[0054]

Examples of the unsaturated dicarboxylic acid compounds include maleic anhydride, maleic acid, maleic acid monoalkyl esters and dialkyl esters, fumaric acid, and fumaric acid monoalkyl esters and dialkyl esters.

[0055]

Examples of the vinyl ester compounds include vinyl acetate, vinyl propionate, vinyl pivalate, vinyl benzoate, and vinyl cinnamate.

[0056]

Examples of the maleimide compounds include maleimide, methylmaleimide, ethylmaleimide, propylmaleimide, butylmaleimide, hexylmaleimide, octylmaleimide, dodecylmaleimide, stearylmaleimide, phenylmaleimide, and cyclohexylmaleimide.

[0057]

The copolymerizable vinyl monomers may be used alone or in combination of two or more. The vinyl monomer is preferably selected according to compatibility of the acrylic block copolymer (A) with the rubber (B), the thermoplastic resin (C), and (or) the thermoplastic elastomer (D). A polymer of methyl methacrylate is depolymerized approximately quantitatively by thermal decomposition. However, in order to suppress depolymerization, the polymer can be copolymerized with an acrylate, for example, methyl acrylate, ethyl acrylate, butyl acrylate, 2-methoxyethyl acrylate, or a mixture thereof, or styrene. In order to further improve oil resistance, the polymer can be copolymerized with acrylonitrile.

[0058]

The glass transition temperature of the methacrylic polymer block (a) is preferably 100°C or more, and more preferably 110°C or more. With the glass transition

temperature of less than 100°C, rubber elasticity at high temperatures easily degrades.

[0059]

The glass transition temperature ( $T_g$ ) of the methacrylic polymer block (a) can be controlled by changing the weight ratio of a constituent monomer of the polymer block according to the Fox's equation.

[0060]

The glass transition temperature is calculated according to the Fox's equation using the ratio of each polymerized monomer and the glass transition temperature of a homopolymer of each constituent monomer which is described in the above-described Polymer Handbook Third Edition.

[0061]

Specific examples of the methacrylic polymer block (a) include the methacrylic polymer blocks contained in the respective acrylic block copolymers produced in Examples 1 to 7 using the acrylic block copolymers produced in Production Examples 1 to 4, the methacrylic polymer block contained in the acrylic block copolymer produced in Production Example 6, and the methacrylic polymer block contained in the amido group-containing acrylic block copolymer produced in Example 8.

[0062]

<Acrylic polymer block (b)>

The constituent monomer of the acrylic polymer block (b) preferably satisfies the relation  $Tg_a > Tg_b$  between the glass transition temperatures of the methacrylic polymer block (a) and the acrylic polymer block (b) which constitute the acrylic block copolymer (A). From the viewpoint of easy production of the acrylic block copolymer (A) having desired physical properties, cost, and availability, the monomer includes 40% by weight to 100% by weight, preferably 50% by weight to 100% by weight, of an acrylate, 0% by weight to 60% by weight, preferably 0% by weight to 50% by weight, of a monomer having a functional group which is a precursor of the acid anhydride group-containing unit (c) or the carboxyl group-containing unit (d), and 0% by weight to 50% by weight, preferably 0% by weight to 25% by weight, of another vinyl monomer copolymerizable therewith. When the ratio of the acrylate is excessively low, the physical properties characteristic of use of an acrylate, particularly compression set, tends to become insufficient.

[0063]

The required molecular weight of the acrylic polymer block (b) may be determined according to the required elastic modulus and rubber elasticity of the acrylic polymer block (b), and the time required for polymerization therefor.

[0064]

The elastic modulus is closely related to the mobility

of a molecular chain (i.e., glass transition temperature) and the molecular weight thereof, and the inherent elastic modulus is not exhibited unless the molecular weight is a certain value or more. This is true for rubber elasticity, but the molecular weight is preferably as large as possible from the viewpoint of rubber elasticity. For example, a range of the required molecular weight  $M_B$  of the acrylic polymer block (b) is preferably  $M_B > 3,000$ , more preferably  $M_B > 5,000$ , further preferably  $M_B > 10,000$ , particularly preferably  $M_B > 20,000$ , and most preferably  $M_B > 40,000$ . However, the polymerization time tends to increase as the number-average molecular weight increases, and thus the molecular weight is preferably 500,000 or less, and more preferably 300,000 or less according to the required productivity.

[0065]

Examples of the acrylate constituting the acrylic polymer block (b) include acrylic acid aliphatic hydrocarbon esters, (for example, alkyl having 1 to 18 carbon atoms) such as methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, isobutyl acrylate, n-pentyl acrylate, n-hexyl acrylate, n-heptyl acrylate, n-octyl acrylate, 2-ethylhexyl acrylate, nonyl acrylate, decyl acrylate, dodecyl acrylate, and stearyl acrylate; acrylic acid alicyclic hydrocarbon esters, such as cyclohexyl acrylate and

isobornyl acrylate; acrylic acid aromatic hydrocarbon esters, such as phenyl acrylate and toluyl acrylate; acrylic acid aralkyl esters, such as benzyl acrylate; acrylic acid esters with functional group-containing alcohols having ether oxygen, such as 2-methoxyethyl acrylate and 3-methoxybutyl acrylate; and acrylic acid fluoroalkyl esters, such as trifluoromethylmethyl acrylate, 2-trifluoromethylethyl acrylate, 2-perfluoroethylacrylate, 2-perfluoroethyl-2-perfluorobutylethyl acrylate, 2-perfluoroethyl acrylate, perfluoromethyl acrylate, diperfluoromethylmethyl acrylate, 2-perfluoromethyl-2-perfluoroethylmethyl acrylate, 2-perfluorohexylethyl acrylate, 2-perfluorodecylethyl acrylate, and 2-perfluorohexadecylethyl acrylate. These acrylates may be used alone or in combination of two or more. Among the acrylates, n-butyl acrylate is preferred from the viewpoint of compression set, cost, and availability. When oil resistance is required, ethyl acrylate is preferred. When low-temperature characteristics are required, 2-ethylhexyl acrylate is preferred. When oil resistance and low-temperature characteristics are desired to be simultaneously satisfied, a mixture of ethyl acrylate, n-butyl acrylate, and 2-methoxyethyl acrylate is preferred.

[0066]

Examples of the vinyl monomer copolymerizable with the constituent methacrylate of the acrylic polymer block (b)

include acrylates, aromatic alkenyl compounds, vinyl cyanide compounds, conjugated diene compounds, halogen-containing unsaturated compounds, unsaturated dicarboxylic acid compounds, vinyl ester compounds, and maleimide compounds.

[0067]

Examples of the methacrylates include methacrylic acid aliphatic hydrocarbon (for example, alkyl having 1 to 18 carbon atoms) esters, such as methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, n-pentyl methacrylate, n-hexyl methacrylate, n-heptyl methacrylate, n-octyl methacrylate, 2-ethylhexyl methacrylate, nonyl methacrylate, decyl methacrylate, dodecyl methacrylate, and stearyl methacrylate; methacrylic acid alicyclic hydrocarbon esters, such as cyclohexyl methacrylate and isobornyl methacrylate; methacrylic acid aralkyl esters, such as benzyl methacrylate; methacrylic acid aromatic hydrocarbon esters, such as phenyl methacrylate and toluyl methacrylate; methacrylic acid esters with functional group-containing alcohols having ether oxygen, such as 2-methoxyethyl methacrylate and 3-methoxybutyl methacrylate; and methacrylic acid fluoroalkyl esters, such as trifluoromethylmethylethyl methacrylate, 2-trifluoromethylethyl methacrylate, 2-perfluoroethylethyl methacrylate, 2-perfluoroethyl-2-perfluorobutylethyl methacrylate, 2-

perfluoroethyl methacrylate, perfluoromethyl methacrylate, diperfluoromethylmethyl methacrylate, 2-perfluoromethyl-2-perfluoroethylmethyl methacrylate, 2-perfluorohexylethyl methacrylate, 2-perfluorodecylethyl methacrylate, and 2-perfluorohexadecylethyl methacrylate.

[0068]

Examples of the aromatic alkenyl compounds include styrene,  $\alpha$ -methylstyrene, p-methylstyrene, and p-methoxystyrene.

[0069]

Examples of the vinyl cyanide compounds include acrylonitrile and methacrylonitrile.

[0070]

Examples of the conjugated diene compounds include butadiene and isoprene.

[0071]

Examples of the halogen-containing unsaturated compounds include vinyl chloride, vinylidene chloride, perfluoroethylene, perfluoropropylene, and vinylidene fluoride.

[0072]

Examples of the unsaturated dicarboxylic acid compounds include maleic anhydride, maleic acid, maleic acid monoalkyl esters and dialkyl esters, fumaric acid, and fumaric acid monoalkyl esters and dialkyl esters.

[0073]

Examples of the vinyl ester compounds include vinyl acetate, vinyl propionate, vinyl pivalate, vinyl benzoate, and vinyl cinnamate.

[0074]

Examples of the maleimide compounds include maleimide, methylmaleimide, ethylmaleimide, propylmaleimide, butylmaleimide, hexylmaleimide, octylmaleimide, dodecylmaleimide, stearylmaleimide, phenylmaleimide, and cyclohexylmaleimide.

[0075]

These copolymerizable monomers may be used alone or in combination of two or more. The vinyl monomer is preferably selected according to the required glass transition temperature, elastic modulus, and polarity of the acrylic polymer block (b), the required physical properties of the acrylic block copolymer (A) used in a composition, and compatibility with the thermoplastic resin and (or) the thermoplastic elastomer. For example, in order to improve oil resistance, the polymer block (b) can be copolymerized with acrylonitrile.

[0076]

The glass transition temperature of the acrylic polymer block (b) is preferably 50°C or less and more preferably 0°C or less. With the glass transition temperature of over 50°C,

the rubber elasticity of the acrylic block copolymer (A) tends to degrade.

[0077]

The glass transition temperature ( $T_g$ ) of the acrylic polymer block (b) can be controlled by changing the weight ratio of each constituent monomer of the polymer block according to the Fox's equation.

[0078]

The glass transition temperature is calculated according to the Fox's equation using the ratio of each polymerized monomer and the glass transition temperature of a homopolymer of each constituent monomer of a polymer block, which is described in the above-described Polymer Handbook Third Edition.

[0079]

Specific examples of the acrylic polymer block (b) include the acrylic polymer blocks contained in the respective acrylic block copolymers produced in Examples 1 to 7 using the acrylic block copolymers produced in Production Examples 1 to 4, the acrylic polymer block contained in the acrylic block copolymer produced in Production Example 6, and the acrylic polymer block contained in the amido group-containing acrylic block copolymer produced in Example 8.

[0080]

<Acid anhydride group-containing unit (c)>

The acid anhydride group-containing unit (c) is characterized in that it has reactivity with a compound having an amino group, a hydroxyl group, an epoxy group, or the like, and thus it can be used as a reactive site for modifying a polymer, as a site for improving compatibility with the rubber, the thermoplastic resin, and (or) the thermoplastic elastomer contained in a blend, or as a cross-linking point for imparting higher rubber elasticity to a soft segment. Since the acid anhydride group-containing unit (c) also has a high glass transition temperature (Tg), the acid anhydride group-containing unit (c) has the effect of improving the heat resistance of the acrylic block copolymer (A) when being introduced into the hard segment. The glass transition temperature of a polymer containing the acid anhydride group-containing unit (c) is high, and for example, the glass transition temperature of polymethacrylic anhydride is as high as 159°C. By introducing a unit containing the unit, the heat resistance of the acrylic block copolymer (A) can be improved.

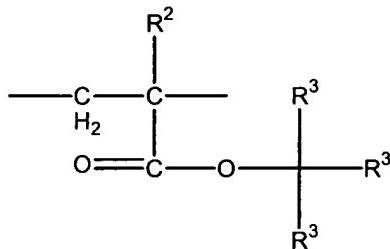
[0081]

As a method for introducing the acid anhydride group-containing unit (c), preferably, a precursor of the acid anhydride group is introduced into the acrylic block copolymer and then cyclized.

As a nonlimiting example, the acid anhydride group-containing unit is preferably introduced by melt-kneading cyclization of an acrylic block copolymer (H) at a temperature of 180°C to 300°C, the block copolymer (H) containing at least one unit represented by formula (2):

[0082]

[Chem. 5]



[0083]

(wherein R<sup>2</sup> represents a hydrogen atom or a methyl group, and R<sup>3</sup>'s each represent a hydrogen atom, a methyl group, or a phenyl group and may be the same or different as long as at least one of R<sup>3</sup>'s is a methyl group).

[0084]

The unit represented by formula (3) can be introduced into the acrylic block copolymer (H) by copolymerization with an acrylate or methacrylate unit represented by formula (2).

[0085]

The unit represented by formula (2) undergoes elimination and cyclization with the adjacent ester unit at

a high temperature to produce, for example, a six-membered ring acid anhydride group (refer to, for example, Hatada, et al., J. M. S. PURE APPL. CHEM., A30 (9&10), PP. 645-667 (1993)). According to this document, a polymer having a bulk ester unit and  $\beta$ -hydrogen generally undergoes decomposition of the ester unit and then cyclization at a high temperature to produce, for example, a six-membered ring acid anhydride group. By using this method, the acid anhydride group can easily be introduced into the acrylic block copolymer (A). Specific examples of such a monomer include, but are not limited to, tert-butyl acrylate, isopropyl acrylate,  $\alpha,\alpha$ -dimethylbenzyl acrylate,  $\alpha$ -methylbenzyl acrylate, tert-butyl methacrylate, isopropyl methacrylate,  $\alpha,\alpha$ -dimethylbenzyl methacrylate, and  $\alpha$ -methylbenzyl methacrylate. Among these monomers, tert-butyl acrylate and tert-butyl methacrylate are preferred from the viewpoint of availability, easy polymerization, and easy production of the acid anhydride group.

[0086]

In order to form the acid anhydride group, the acrylic block copolymer (H) is preferably heated at a high temperature of 180°C to 300°C. With heating at a temperature of lower than 180°C, the acid anhydride group tends not to be sufficiently produced, while with heating at a temperature of over 300°C, the polymer (H) tends to be

decomposed.

[0087]

<Carboxyl group-containing unit (d)>

The carboxyl group-containing unit (d) has high cohesive force, and a polymer of a carboxyl group-containing monomer has a high glass transition temperature (Tg) and thus has the effect of improving the heat resistance of a block copolymer. Although a functional group such as a hydroxyl group also has a hydrogen bonding ability, the functional group has low Tg and has the small effect of improving heat resistance, as compared with a monomer containing a carboxyl group. Therefore, from the viewpoint of further improvements in heat resistance and cohesive force of the acrylic block copolymer, the acrylic block copolymer may contain the carboxyl group-containing unit (d).

[0088]

A method for introducing the carboxyl group-containing unit (d) is not particularly limited, but the carboxyl group-containing unit (d) is preferably produced in the process for introducing the acid anhydride group-containing unit (c) into the acrylic block copolymer (A).

[0089]

The method will be described below.

[0090]

In a method for producing the carboxyl group-containing

unit (d) in the process for introducing the acid anhydride group-containing unit (c) into the acrylic block copolymer (A), the block copolymer (H) having a unit represented by formula (2) is heated at, for example, 180°C to 300°C, to introduce the acid anhydride group-containing unit (c), but the carboxyl group-containing unit (d) can be introduced by controlling the heating temperature and time and the content of the unit represented by formula (2). The unit represented by formula (2) undergoes elimination and cyclization with the adjacent ester unit at a high temperature to produce an acid anhydride group (refer to, for example, Hatada, et al., J. M. S. PURE APPL. CHEM., A30 (9&10), PP. 645-667 (1993)). In this case, the ester units partially take a path comprising decomposition of the ester unit to produce a carboxyl group, and then cyclization to produce an acid anhydride group. By utilizing this path, the carboxyl group-containing (d) can be introduced by appropriately controlling the heating temperature and time according to the type and content of the unit represented by formula (2). The carboxyl group-containing unit (d) tends to cyclize with the adjacent ester unit at a high temperature, and thus the physical properties after molding tend to change, thereby causing difficulty in producing products with stable physical properties.

[0091]

A polymer having a carboxyl group has a high glass transition temperature, and for example, polymethacrylic acid has a glass transition temperature of as high as 228°C. Therefore, the heat resistance of the acrylic block copolymer can be improved by introducing a monomer constituting such a polymer.

[0092]

<Process for producing acrylic block copolymer (H)>

Although the process for producing the acrylic block copolymer (H) is not particularly limited, controlled polymerization using a initiator for polymerization is preferably performed.

[0093]

Examples of the controlled polymerization include living anionic polymerization, radical polymerization using a chain transfer agent, and living radical polymerization recently developed. In particular, living radical polymerization is preferred from the viewpoint of control of the molecular weight and structure of the block copolymer.

[0094]

The living radical polymerization is radical polymerization in which the activity of the polymerization terminal is maintained without a loss. In a narrow sense, living polymerization represents polymerization in which the terminal continuously possesses activity. However, living

polymerization generally includes pseudo living polymerization in which inactivated terminals are equilibrium with activated terminals. In the present invention, the meaning of living polymerization includes the pseudo living polymerization. In recent years, living radical polymerization has been actively studied by various groups.

[0095]

Examples of living radical polymerization include polymerization using a polysulfide as a chain transfer agent, polymerization using a cobalt porphyrin complex (Journal of the American Chemical Society (J. Am. Chem. Soc.), 1994, vol. 116, p. 7943) or a nitroxide compound as a radical scavenger (Macromolecules, 1994, vol. 27, p. 7228), and atom transfer radical polymerization (ATRP) using an organic halide as an initiator and a transition metal complex as a catalyst. In the present invention, any one of these polymerization methods can be used, but atom transfer radical polymerization is preferred from the viewpoint of ease of control.

[0096]

The atom transfer radical polymerization is performed using an organic halide or a sulfonyl halide compound as an initiator, and using a metal complex including a central metal selected from the elements of Groups VIII, IX, X, or

XI of the periodic table as a catalyst (refer to, for example, Matyjaszewski, et al., Journal of the American Chemical Society (J. Am. Chem. Soc.), 1995, Vol. 117, p. 5614, Macromolecules, 1995, Vol. 28, p. 7901, Science, 1996, Vo. 272, p. 866, or Sawamoto, et al., Macromolecules, 1995, Vol. 28, p. 1721).

[0097]

In radical polymerization methods, the polymerization rate is generally very high, and termination reaction such as coupling between radicals or the like easily occurs. However, in above-mentioned method polymerization proceeds in a living state to produce a polymer having a narrow molecular weight distribution ( $M_w/M_n = 1.1$  to  $1.5$ ), and the molecular weight can be freely controlled by the changing ratio of the monomer to the initiator.

[0098]

In the atom transfer radical polymerization, a mono-, di- or higher-functional compound can be used as the organic halide or the sulfonyl halide compound serving as the initiator. These compounds may be appropriately used according to purposes. However, a monofunctional compound is preferably used for producing a diblock copolymer from the viewpoint of availability of the initiator, and a difunctional compound is preferably used for producing an (A-B-A)-triblock copolymer or (B-A-B)-triblock copolymer

from the viewpoint of the number of the reaction steps and the short reaction time. A polyfunctional compound is preferably used for producing a branched block copolymer from the viewpoint of the number of the reaction steps and the short reaction time.

[0099]

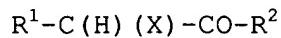
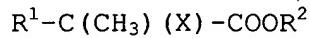
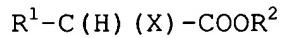
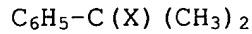
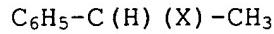
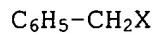
A polymeric initiator can also be used as the initiator.

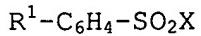
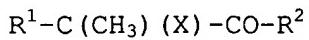
[0100]

The macroinitiator is a compound among the organic halide and the sulfonyl halide compound, and comprises a polymer having a halogen atom bonded to an end of its molecular chain. Such a macroinitiator can be produced by a controlled polymerization method other than the living radical polymerization method, it is possible to produce a block copolymer comprising polymers bonded together and produced by different polymerization methods.

[0101]

Examples of the monofunctional compound include the following:





(wherein  $C_6H_5$  represents a phenyl group,  $C_6H_4$  represents a phenylene group (which may be ortho-substituted, meta-substituted, or para-substituted),  $R^1$  represents a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms,  $X$  represents chlorine, bromine, or iodine, and  $R^2$  represents a monovalent organic group having 1 to 20 carbon atoms).

[0102]

Examples of an alkyl group (including an alicyclic hydrocarbon group) having 1 to 20 carbon atoms as  $R^1$  include methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, n-hexyl, cyclohexyl, n-heptyl, n-octyl, 2-ethylhexyl, nonyl, decyl, dodecyl, and isobornyl. Examples of an aryl group having 6 to 20 carbon atoms include phenyl, toluyl, and naphthyl. Examples of an aralkyl group having 7 to 20 carbon atoms include benzyl and phenetyl.

[0103]

Examples of a monovalent organic group having 1 to 20 carbon atoms as  $R^2$  include the same as those of  $R^1$ .

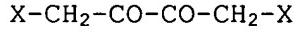
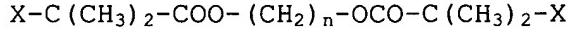
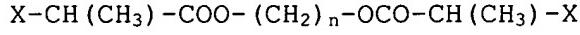
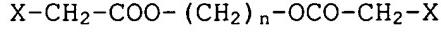
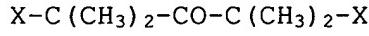
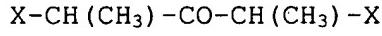
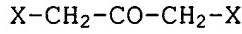
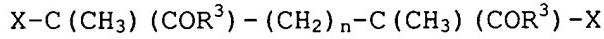
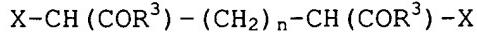
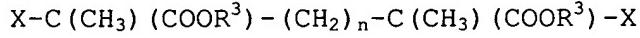
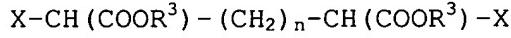
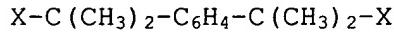
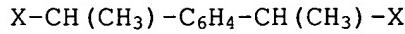
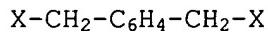
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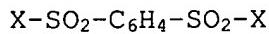
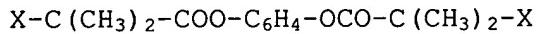
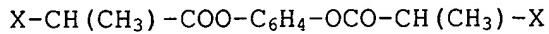
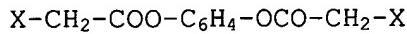
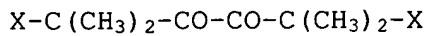
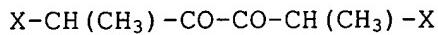
Specific examples of the monofunctional compound include tosyl bromide, methyl 2-bromopropionate, ethyl 2-

bromopropionate, butyl 2-bromopropionate, methyl 2-bromoisobutyrate, ethyl 2-bromoisobutyrate, and butyl 2-bromoisobutyrate. Among these compounds, ethyl 2-bromopropionate and butyl 2-bromopropionate are preferred from the viewpoint that polymerization can easily be controlled because the structures are similar to that of an acrylate monomer.

[0105]

Examples of the difunctional compound include the following:





(wherein R<sup>3</sup> represents alkyl having 1 to 20 carbon atoms, aryl having 6 to 20 carbon atoms, or aralkyl having 7 to 20 carbon atoms, and n represents an integer of 0 to 20. C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>4</sub>, and X represent the same as the above).

[0106]

Specific examples of alkyl having 1 to 20 carbon atoms, aryl having 6 to 20 carbon atoms, and aralkyl having 7 to 20 carbon atoms as R<sup>3</sup> are the same as those of alkyl having 1 to 20 carbon atoms, aryl having 6 to 20 carbon atoms, and aralkyl having 7 to 20 carbon atoms as R<sup>1</sup>.

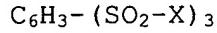
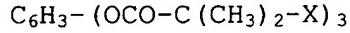
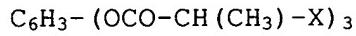
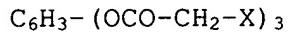
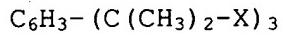
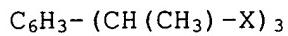
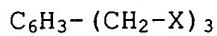
[0107]

Specific examples of the difunctional compound include bis(bromomethyl)benzene, bis(1-bromoethyl)benzene, bis(1-bromoisopropyl)benzene, dimethyl 2,3-dibromosuccinate, diethyl 2,3-dibromosuccinate, dibutyl 2,3-dibromosuccinate, dimethyl 2,4-dibromoglutamate, diethyl 2,4-dibromoglutamate, dibutyl 2,4-dibromoglutamate, dimethyl 2,5-dibromoadipate, diethyl 2,5-dibromoadipate, dibutyl 2,5-dibromoadipate, dimethyl 2,6-dibromopimelate, diethyl 2,6-dibromopimelate,

dibutyl 2,6-dibromopimelate, dimethyl 2,7-dibromosuberate, diethyl 2,7-dibromosuberate, and dibutyl 2,7-dibromosuberate. Among these compounds, bis(bromomethyl)benzene, diethyl 2,5-dibromo adipate, and diethyl 2,6-dibromopimelate are preferred from the viewpoint of availability of raw materials.

[0108]

Examples of the polyfunctional compound include the following:



(wherein  $C_6H_3$  represents a trivalent phenyl group (having any desired combination of three bonding positions among the 1-to 6-position), and X represents the same as the above).

[0109]

Specific examples of the polyfunctional compound include tris(bromomethyl)benzene, tris(1-bromoethyl)benzene, and tris(1-bromoisopropyl)benzene. Among these compounds, tris(bromomethyl)benzene is preferred from the viewpoint of availability of raw materials.

[0110]

When an organic halide or sulfonyl halide compound having a functional group other than a polymerization initiating group is used, a polymer having a functional group other than the polymerization initiating group in its end or its molecule can be obtained. Examples of a functional group other than the polymerization initiating group include alkenyl, hydroxyl, epoxy, amino, amido, and silyl.

[0111]

The organic halide or sulfonyl halide compound which can be used as the initiator has a carbon atom bonded to a halogen group (halogen atom) and to a carbonyl or phenyl group, and a carbon-halogen bond is activated to initiate polymerization. The amount of the initiator used may be determined from a molar ratio to the monomer used according to the required molecular weight of the acrylic block copolymer. Namely, the molecular weight of the acrylic block copolymer can be controlled by controlling the number of the monomer molecules used per molecule of the initiator.

[0112]

Although the transition metal complex used as the catalyst for the atom transfer radical polymerization is not particularly limited, complexes of mono- or zero-valent copper, divalent ruthenium, divalent iron, and divalent

nickel are preferably used. Among these complexes, copper complexes are preferred from the viewpoint of cost and reaction controllability.

[0113]

Examples of monovalent copper compounds include cuprous chloride, cuprous bromide, cuprous iodide, cuprous cyanide, cuprous oxide, and cuprous perchlorate. Among these compounds, cuprous chloride and cuprous bromide are preferred from the viewpoint of polymerization controllability. When a monovalent copper compound is used, a ligand may be added for increasing catalytic activity. Examples of such a ligand include 2,2'-bipyridyl compounds, such as 2,2'-bipyridyl and its derivatives (for example, 4,4'-dinoryl-2,2'-bipyridyl and 4,4'-di(5-noryl)-2,2'-bipyridyl); 1,10-phenanthroline compounds, such as 1,10-phenanthroline and its derivatives (for example, 4,7-dinoryl-1,10-phenanthroline and 5,6-dinoryl-1,10-phenanthroline); and polyamines, such as tetramethyldiethylenetriamine (TMEDA), pentamethyldiethylenetriamine, and hexamethyl(2-aminoethyl)amine.

[0114]

Also, a tristriphenylphosphine complex ( $\text{RuCl}_2(\text{PPh}_3)_3$ ) of divalent ruthenium chloride is preferred as the catalyst. When a ruthenium compound is used as the catalyst, an aluminum alkoxide may be added as an activating agent.

Furthermore, a bistriphenylphosphine complex ( $\text{FeCl}_2(\text{PPh}_3)_2$ ) of divalent iron, a bistriphenylphosphine complex ( $\text{NiCl}_2(\text{PPh}_3)_2$ ) of divalent nickel, and a bistributylphosphine complex ( $\text{NiBr}_2(\text{PBu}_3)_2$ ) of divalent nickel are preferred as the catalyst.

[0115]

Although the types of the catalyst, ligand, and activating agent used are not particularly limited, the types may be properly determined from the relation between the required reaction rate and the types of the initiator, monomer, and solvent used. For example, when an acrylic monomer such as an acrylate or the like is used for polymerization, a propagation end of a polymer chain preferably has a carbon-bromine bond from the controllability of polymerization. Therefore, preferably, an organic bromide or sulfonyl bromide is used as the initiator, acetonitrile is used as the solvent, a metal complex including copper or copper bromide, preferably cuprous bromide, as a central metal is used as the catalyst, and pentamethyldiethylenetriamine or the like is used as the ligand. On the other hand, when a methacrylic monomer such as a methacrylate or the like is used for polymerization, a propagation end of a polymer chain preferably has a carbon-chlorine bond from the controllability of polymerization. Therefore, preferably, an organic chloride or sulfonyl

chloride is used as the initiator, acetonitrile, and if required, a mixture with toluene, is used as the solvent, a metal complex including copper or copper chloride, preferably cuprous chloride, as a central metal is used as the catalyst, and pentamethyldiethylenetriamine or the like is used as the ligand.

[0116]

The amounts of the catalyst and ligand used may be properly determined from the relation between the required reaction rate and the amounts of the initiator, monomer, and solvent used. For example, when a polymer having a high molecular weight is desired, the initiator/monomer ratio must be lower than that for producing a polymer having a low molecular weight. In this case, the reaction rate can be increased by increasing the amounts of the catalyst and ligand used. Also, when a polymer having a higher glass transition temperature than room temperature is produced, in some cases, an appropriate organic solvent is added for decreasing the viscosity of the system and increasing the efficiency of stirring, and thus the reaction rate tends to decrease. In this case, the reaction rate can be increased by increasing the amounts of the catalyst and ligand used.

[0117]

The atom transfer radical polymerization can be performed without a solvent (bulk polymerization) or in any

of various solvents. The bulk polymerization or polymerization in any of various solvents can be stopped during the reaction.

[0118]

Examples of the solvent include hydrocarbon solvents, ether solvents, halogenated hydrocarbon solvents, ketone solvents, alcohol solvents, nitrile solvents, ester solvents, and carbonate solvents.

[0119]

Examples of the hydrocarbon solvents include benzene and toluene. Examples of the ether solvents include diethyl ether and tetrahydrofuran. Examples of the halogenated hydrocarbon solvents include methylene chloride and chloroform. Examples of the ketone solvents include acetone, methyl ethyl ketone, and methyl isobutyl ketone. Examples of the alcohol solvents include methanol, ethanol, propanol, isopropanol, n-butanol, and tert-butanol. Examples of the nitrile solvents include acetonitrile, propionitrile, and benzonitrile. Examples of the ester solvents include ethyl acetate and butyl acetate. Examples of the carbonate solvents include ethylenecarbonate and propylene carbonate. These solvents may be used alone or in combination of two or more.

[0120]

When the solvent is used, the amount of the solvent

used may be properly determined based on the relation between the viscosity of the whole system and the required efficiency of stirring (i.e., reaction rate). When bulk polymerization or polymerization in a solvent is stopped during the reaction, the conversion rate of the monomer at the reaction stop point may be properly determined based on the relation between the viscosity of the whole system and the required efficiency of stirring (i.e., reaction rate).

[0121]

The polymerization can be performed in the range of room temperature to 200°C and preferably 50°C to 150°C.

[0122]

Examples of a method for producing the acrylic block copolymer by the polymerization include a method of successively adding monomers, a method of polymerizing a monomer for a second block using a previously synthesized polymer as a macroinitiator, and a method of bonding different polymers by reaction, the polymers being separately produced by polymerization. Any one of these methods may be properly used according to purposes. In view of simplicity of the production process, the method of successively adding monomers is preferably used. When it is desired to avoid a remaining monomer of a first block from being copolymerized with a second block, the method of polymerizing a monomer of the second block using the

previously synthesized polymer as the macroinitiator is preferably used.

[0123]

Detailed description will be made of the method of successively adding monomers, and the method of polymerizing a monomer of the second block using the previously synthesized polymer as the macroinitiator. However, the method for producing the acrylic block copolymer of the present invention is not limited to these methods.

[0124]

In the method of successively adding monomers, the second monomer to be polymerized is preferably charged when the conversion ratio of the first monomer to be polymerized reaches 80% to 95%. When polymerization proceeds until the conversion ratio exceeds 95% (for example, 96% to 100%), the propagation reaction of a polymer chain is inhibited with high probability. There is also the tendency that polymer radicals readily react with each other to easily cause side reactions such as disproportionation, coupling, chain transfer, and the like. When the second monomer to be polymerized is charged at a conversion ratio of less than 80% (for example, 79% or less), the first monomer to be polymerized may be disadvantageously mixed and copolymerized with the second monomer to be polymerized.

[0125]

In this case, possible methods for adding in order the monomers include a method (x1) in which an acrylic monomer is first charged and polymerized, and then a methacrylic monomer is charged and polymerized, and a method (y1) in which a methacrylic monomer is first charged and polymerized, and then an acrylic monomer is charged and polymerized. The method (x1) in which an acrylic monomer is first charged and polymerized, and then a methacrylic monomer is charged and polymerized is preferred from the viewpoint of controllability of polymerization. This is because it is preferable that the methacrylic polymer block is propagated from the end of the acrylic polymer block.

[0126]

As a possible example of the method of polymerizing a monomer of the second block using the previously synthesized polymer as the macroinitiator, polymerization of a monomer of the first block is stopped at a desired point by decreasing the temperature in a living state, and a monomer of the second block is added after the monomer of the first block is removed by distillation or the like under reduced pressure. When polymerization of monomer of a third block is desired, the same operation as that for the second block may be performed. This method can avoid the remaining monomer of the previous block from being copolymerized in polymerization of a monomer of the subsequent block.

[0127]

In this case, possible methods for polymerizing in order the monomers of the blocks include a method (x2) in which an acrylic block is first produced by polymerization, and then a methacrylic block is produced by polymerization, and a method (y2) in which a methacrylic block is produced by polymerization, and then an acrylic block is produced by polymerization. The method (x2) in which an acrylic block is first produced by polymerization, and then a methacrylic block is produced by polymerization is preferred from the viewpoint of controllability of polymerization. This is because it is preferable that the methacrylic polymer block be propagated from the end of the acrylic polymer block.

[0128]

Next, a method for determining the conversion rate of the acrylic monomer, the methacrylic monomer, or the like will be described.

[0129]

In order to determine the conversion rate, a gas chromatographic (GC) method, a weight method, or the like can be used.

[0130]

In the GC method, reaction solutions are sampled from the polymerization system before initiation of the reaction and any time in the course of the reaction and subjected to

GC measurement, and the consumption rate of a monomer is determined from the existence ratio of the monomer to the internal standard previously added to the polymerization system. This method is advantageous in that even when a plurality of monomers is present in the system, the conversion ratios can be independently determined. In the weight method, a reaction solution is sampled from the polymerization system, and a solid concentration is determined from the weights before and after drying to determine the overall conversion ratio of monomers. This method is advantageous in that the conversion ratio can easily be determined. Of these methods, the GC method is preferred for a case in which a plurality of monomers is present in the system, for example, the acrylic monomer is present as a co-monomer for the methacrylic monomer.

[0131]

The reaction solution obtained by polymerization contains a mixture of a polymer and a metal complex. Therefore, an organic acid containing a carboxyl group or a sulfonyl group is added to the reaction solution to produce a metal salt with the metal complex so that the metal complex can be removed as a solid by filtration or the like. Then, the impurities such as the acid remaining in the solution are removed by adsorption on basic activated alumina, a basic adsorbent, a solid inorganic acid, an anion

exchange resin, or a cellulose anion exchanger to produce a solution of the acrylic block copolymer.

[0132]

Then, the polymerization solvent and unreacted monomers remaining in the thus-obtained acrylic block copolymer solution are removed by evaporation to isolate the acrylic block copolymer.

[0133]

As the evaporation method, a thin-film evaporation method, a flash evaporation method, a horizontal evaporation method using an extrusion screw, or the like can be used. Since the acrylic block copolymer has tackiness, evaporation can be efficiently performed by the horizontal evaporation method using the extrusion screw among these evaporation methods, or by combination of the horizontal evaporation method with another evaporation method.

[0134]

<Process for producing acrylic block copolymer (A)>

A preferred process for producing the acrylic block copolymer (A) comprises heating the acrylic block copolymer (H) at a high temperature of 180°C to 300°C. In this process, the acrylic block copolymer (H) may be heated in the state of the polymer solution under pressure, heated while being subjected to evaporation for removing the solvent from the polymer solution, or directly heat-melted.

However, from the viewpoint of reactivity to the acid anhydride group and simplicity of production, the acrylic block copolymer (H) is preferably directly heat-melted. The acrylic block copolymer (H) is more preferably melt-kneaded.

[0135]

The method of heating the acrylic block copolymer (H) in the state of the polymer solution can be performed using a pressure-resistant reactor.

[0136]

The method of heating the acrylic block copolymer (H) while removing the solvent from the polymer solution by evaporation can be performed by the horizontal evaporation method using the extrusion screw.

[0137]

The method of directly heat-melting the acrylic block copolymer (A') can be performed using a pressing machine or an injection molding machine.

[0138]

The acrylic block copolymer (H) may be melt-kneaded by any of various apparatuses capable of heating and kneading at the same time. Examples of such apparatuses include apparatuses ordinarily used for processing rubber, such as a Banbury mixer, a kneader, and a single-screw or multi-screw extruder. An extruder is preferably used in view of reactivity to the acid anhydride group, and simplicity of

production. When the acrylic block copolymer (H) is melt-kneaded, the melt-kneading time (retention time in an extruder if the extruder is used) may be appropriately determined according to the melt-kneading temperature, the configuration of the screw, L/D (effective length L of the screw/diameter D of the screw), the screw rotational speed, etc.

[0139]

<Method for conversion to carboxyl group-containing unit (d)>

Like in the method for introducing the acid anhydride group-containing unit (c), in the method for producing the carboxyl group-containing unit (d) in the process for introducing the acid anhydride group-containing unit (c) into the acrylic block copolymer (A), the acrylic block copolymer (H) may be heated in the state of the polymer solution under pressure or may be directly heat-melted. From the viewpoint of simplicity of the production, the acrylic block copolymer (H) is preferably melt-kneaded.

[0140]

When the acrylic block copolymer (H) is melt-kneaded, the melt-kneading time (retention time in an extruder if the extruder is used) may be appropriately determined according to the melt-kneading temperature, the configuration of the screw, L/D (effective length L of the screw/diameter D of

the screw), the screw rotational speed, etc.

[0141]

<Carboxyl group-containing unit (e)>

When the acrylic block copolymer (A) is required to have higher heat resistance as a seal product, the carboxyl group-containing unit (e) may be introduced. A polymer having a carboxyl group has a high glass transition temperature, and for example, polymethacrylic acid has a glass transition temperature of as high as 228°C. Therefore, the heat resistance of the block copolymer can be further improved by increasing the amount of the constituent monomer of such a polymer.

[0142]

The carboxyl group-containing unit (e) can be preferably introduced by hydrolytic ring-opening of the acid anhydride group-containing unit (c) of the acrylic block copolymer (A).

[0143]

The method for introducing the carboxyl group-containing unit (e) by hydrolyzing the acid anhydride group-containing unit (c) is not particularly limited. The acrylic block copolymer (A) may be heated together with water under pressure or melt-kneaded together with water. In view of simplicity of the production and cost, the acrylic block copolymer (A) is preferably melt-kneaded

together with water.

[0144]

As the method of heating the acrylic block copolymer (A) together with water under pressure, the copolymer (A) may be heated in a pressure-resistant reactor.

[0145]

As the method for melt-kneading the acrylic block copolymer (A) together with water, the copolymer (A) may be melt-kneaded by any of various apparatuses capable of heating and kneading at the same time. Examples of such apparatuses include apparatuses ordinarily used for processing rubber, such as a Banbury mixer, a kneader, and a single-screw or multi-screw extruder. In view of reactivity to the acid anhydride group, and simplicity of production, an extruder is preferably used, and a closed extruder is more preferably used.

[0146]

When the acrylic block copolymer (A) is melt-kneaded together with water, the melt-kneading time (retention time in an extruder if the extruder is used) may be appropriately determined according to the melt-kneading temperature, the configuration of the screw, L/D (effective length L of the screw/diameter D of the screw), the screw rotational speed, etc.

[0147]

The carboxyl group-containing unit (e) is produced by hydrolyzing an acid anhydride group in the acid anhydride group-containing unit (c), but the carboxyl group-containing unit (e) need not be discriminated from the carboxyl group-containing unit (d) produced in the process for introducing the acid anhydride group-containing unit (c). The total content of monomers containing the carboxyl group-containing units (d) and (e) may be 50% by weight or less of the constituent monomers of the acrylic block copolymer (A). The content of the carboxyl group-containing units may be appropriately determined according to the required physical properties of the acrylic block copolymer (A) used for a seal product.

[0148]

<Composition>

The acrylic block copolymer (A) used in the present invention may be used for producing seal products or combined with the crosslinked and (or) uncrosslinked rubber (B), the thermoplastic resin (C), and (or) the thermoplastic elastomer (D), or a lubricant (E) and (or) an inorganic filler (F) to produce compositions for producing seal products. Alternatively, the acrylic block copolymer (A) may be combined with the crosslinked and (or) uncrosslinked rubber (B) or the thermoplastic resin (C) and (or) the thermoplastic elastomer (D), and a lubricant (E) and (or) an

inorganic filler (F) to produce compositions for producing seal products.

[0149]

Methods for mixing the acrylic block copolymer (A) with the crosslinked and (or) uncrosslinked rubber (B), the thermoplastic resin (C) and (or) the thermoplastic elastomer (D), and the lubricant (E) and (or) the inorganic filler (F) includes the following: a method in which the crosslinked and (or) uncrosslinked rubber (B) is added to the acrylic block copolymer (A) to improve the physical properties thereof, such as low-temperature properties; a method in which the acrylic block copolymer (A) is added to the crosslinked rubber (B) to impart thermoplasticity to the crosslinked rubber and improve the processability and recycle property of the crosslinked rubber (B); a method in which the thermoplastic resin (C) and the thermoplastic elastomer (D) are added to the acrylic block copolymer (A) to improve the physical properties thereof, such as mechanical properties, hardness, and low-temperature properties; a method in which the acrylic block copolymer (A) is added as a softener to the thermoplastic resin (C) and the thermoplastic elastomer (D) to improve the hardness and compression set of the thermoplastic resin (C) and (or) the thermoplastic elastomer (D) while maintaining the high elastic modulus; and a method in which the acrylic block

copolymer (A) is added as a compatibilizer to at least two types of the thermoplastic resin (C) and (or) the thermoplastic elastomer (D) to improve mechanical properties by utilizing the reactivity of the acrylic block copolymer (A).

[0150]

The lubricant (E) and the inorganic filler (G) are added to the acrylic block copolymer (A) to decrease the resin surface frictionality of the acrylic block copolymer (A) and to improve the mechanical properties, such as elastic modulus, and processability.

[0151]

The mixing ratios of the acrylic block copolymer (A) to the crosslinked and (or) uncrosslinked rubber (B), the thermoplastic resin (C) and (or) the thermoplastic elastomer (D), and to the lubricant (E) and (or) the inorganic filler (F) may be appropriately determined according to the required physical properties of various seal products. For example, when the acrylic block copolymer (A) is added for improving workability of crosslinked rubber or a seal product, such as an automobile glass run channel or the like, in which the low-temperature characteristics of the acrylic block copolymer (A) must be improved, 0.5% by weight to 99.5% by weight, more preferably 0.5% by weight to 90% by weight, of the acrylic block copolymer (A) is preferably

mixed with 99.5% by weight to 0.5% by weight, more preferably 99.5% by weight to 10% by weight, of the crosslinked and (or) uncrosslinked rubber (B). When the content of the acrylic block copolymer (A) is less than 0.5% by weight, the workability of the crosslinked rubber tends not to be sufficiently improved. When the content of the crosslinked rubber (B) is less than 0.5% by weight, the low-temperature properties of the acrylic block copolymer (A) tend not to be sufficiently improved.

[0152]

When the thermoplastic resin (C) and (or) the thermoplastic elastomer is added to the acrylic block copolymer (A), preferably 0.5% by weight to 99.5% by weight, more preferably 0.5% by weight to 90% by weight, of the acrylic block copolymer (A) is mixed with preferably 99.5% by weight to 0.5% by weight, more preferably 99.5% by weight to 10% by weight, of the thermoplastic resin (C) and (or) the thermoplastic elastomer (D). When the content of the acrylic block copolymer (A) is less than 0.5% by weight, the physical properties of the thermoplastic resin (C) and (or) the thermoplastic elastomer (D), such as mechanical properties and hardness, tend not to be sufficiently improved. When the content of the thermoplastic resin (C) and (or) the thermoplastic elastomer (d) is less than 10% by weight, the physical properties of the acrylic block

copolymer (A), such as the mechanical properties and hardness, tend not to be sufficiently improved.

[0153]

When the lubricant (E) and (or) the inorganic filler (F) are added to the acrylic block copolymer (A), the contents of the lubricant (E) and the inorganic filler (F) are preferably 0.01 parts to 50 parts and 0.01 parts to 300 parts, and more preferably 0.1 parts to 30 parts and 0.1 parts to 100 parts, respectively, relative to 100 parts by weight of the total of the acrylic block copolymer (A) and the crosslinked and (or) uncrosslinked rubber (B) or the acrylic block copolymer (A), the thermoplastic resin (C), and (or) the thermoplastic elastomer. When the content of the lubricant (E) is less than 0.1 parts, resin surface frictionality tends to increase. When the content of the lubricant (E) exceeds 50 parts, the lubricant tends to bleed out. When the content of the inorganic filler (F) is less than 0.01 parts, the mechanical properties such as elastic modulus tend to become unsatisfactory. When the content of the inorganic filler (F) exceeds 300 parts, tensile elongation tends to decrease, or compression set tends to degrade.

[0154]

<Rubber (B)>

In the present invention, the crosslinked rubber among

the crosslinked and (or) uncrosslinked rubber (B) is vulcanized rubber prepared by vulcanizing unvulcanized rubber, or core-shell rubber crosslinked with a graft crosslinking agent or the like. The uncrosslinked rubber is unvulcanized rubber which is not crosslinked by vulcanization. When the crosslinked rubber is used, it can desirably easily blended and then molded. When the uncrosslinked rubber is used, flexibility can be desirably imparted without using a plasticizer which has a problem in recycle. In particular, the uncrosslinked rubber and the acrylic block copolymer (A) are preferably dynamically heat-treated to prepare a rubber-containing composition because the degree of crosslinking can be freely controlled.

[0155]

The term "dynamically heat-treated" means kneading in a melting state. According to development by W. Fisher et al. of Uniroyal Co. and A. Y. Coran et al. of Monsanto Co., uncrosslinked rubber is blended with a matrix of a thermoplastic resin or a thermoplastic elastomer, and the resultant blend is kneaded with a crosslinking agent at a temperature higher than the crosslinking temperature of the crosslinking agent to highly crosslink the rubber and finely disperse the rubber.

[0156]

Examples of the crosslinked and (or) uncrosslinked

rubber (B) include acrylic rubber (ACM), ethylene-acrylate copolymer rubber (AEM), acrylonitrile-acrylate copolymer rubber (ANM), chlorinated polyethylene (CM), chlorosulfonated polyethylene (CSM), ethylene-propylene copolymer rubber (EPM), ethylene-propylene-diene copolymer rubber (EPDM), ethylene-vinyl acetate copolymer rubber (EVA), tetrafluoroethylene-propylene rubber (FEPM), tetrafluoroethylene-propylene-vinylidene fluoride rubber, fluororubber (FKM), polyisobutylene (PIB), epichlorohydrin rubber (CO), acrylate-butadiene rubber (ABR), styrene-butadiene rubber (SBR), butadiene rubber (BR), natural rubber (NR), epoxidized natural rubber (ENR), isoprene rubber (IR), butyl rubber (IIR), brominated butyl rubber (BIIR), chlorinated butyl rubber (CIIR), acrylonitrile-butadiene copolymer rubber (NBR), hydrogenated nitrile rubber (H-NBR), chloroprene rubber, norbornene rubber (NOR), polyester urethane rubber (AU), polyether urethane rubber (EU), silicone rubber (VMQ), fluorosilicone rubber (FVMQ), polydimethylsiloxane (MQ), polysulfide rubber, ethylene-methyl acrylate copolymer rubber (EMA), ethylene-ethyl acrylate copolymer rubber (EEA), and ethylene-methyl methacrylate copolymer rubber (EMMA). Examples of the core-shell type crosslinked rubber having excellent compatibility with other resins include, but are not limited to, commercially available products, such as KaneAce (produced

by Kanegafuchi Chemical Industry Co., Ltd.) and Metablen (Mitsubishi Rayon Co., Ltd.). These rubber materials may be used alone or in combination of two or more. Among these rubber materials, silicone rubber (VMQ) is preferred from the viewpoint of excellent low-temperature properties and high-temperature properties (heat resistance) required for various seal products. Also, core-shell silicone rubber including a core made of silicone and a shell made of methyl methacrylate or the like is preferred because it further has mechanical properties. Another rubber having high compatibility with the acrylic block copolymer (A) can also be preferably used.

[0157]

<Thermoplastic resin (C)>

Examples of resins usable as the thermoplastic resin (C) in the present invention include polyvinyl chloride resins, polyethylene resins, polypropylene resins, cyclic olefin copolymer resins, polymethyl methacrylate resins, polystyrene resins, polyphenylene ether resins, polycarbonate resins, polyester resins, polyamide resins, polyacetal resins, polyphenylene sulfide resins, polysulfone resins, polyimide resins, polyetherimide resins, polyether ketone resins, polyetherether ketone resins, and polyamide-imide resins. These resins may be used alone or in combination of two or more. Among these resins, a resin

having high compatibility with the acrylic block copolymer (A) is preferably used, and a resin having a functional group reactive with an acid anhydride group is more preferably used. Examples of a functional group reactive with an acid anhydride group include an amino group and a hydroxyl group. Examples of a thermoplastic resin having such a functional group include polyester resins and polyamide resins. Other thermoplastic resins each having a functional group reactive with an acid anhydride group can also be preferably used.

[0158]

The thermoplastic resin (C) is preferably dynamically heat-treated together with the acrylic block copolymer (A) because the heat resistance, oil resistance, and low-temperature brittleness of the acrylic block copolymer (A) can be improved.

[0159]

<Thermoplastic elastomer (D)>

Examples of thermoplastic elastomers usable as the thermoplastic elastomer (D) in the present invention include a styrene elastomer, an olefin elastomer, an urethane elastomer, a vinyl chloride elastomer, an ester elastomer, an amide elastomer, and an acrylic elastomer. These elastomers may be used alone or in combination of two or more. Among these elastomers, the acrylic elastomer is

preferred from the viewpoint of oil resistance, heat resistance, and compatibility, and the ester elastomer and the amide elastomer are preferred from the viewpoint of oil resistance, heat resistance, and the presence of a functional group reactive to an acid anhydride group. Other thermoplastic elastomers having functional groups reactive to an acid anhydride group can also be preferably used.

[0160]

The thermoplastic elastomer (D) is preferably dynamically heat-treated together with the acrylic block copolymer (A) because the oil resistance, heat resistance, weather resistance, and flaw resistance can be imparted while the elastomer properties, such as flexibility, is maintained.

[0161]

<Lubricant (E)>

Examples of materials usable as the lubricant (E) in the present invention include, but are not limited to, fatty acids, such as stearic acid and palmitic acid; fatty acid metal salts, such as calcium stearate, zinc stearate, magnesium stearate, potassium palmitate, and sodium palmitate; waxes, such as polyethylene wax, polypropylene wax, and montan wax; low-molecular-weight polyolefins, such as low-molecular-weight polyethylene and low-molecular-weight polypropylene; polyorganosiloxane, such as

dimethylpolysiloxane; octadecylamine; alkyl phosphates; fatty acid esters; amide lubricants, such as ethylene bis-stearyl amide; fluororesin powders, such as tetrafluoroethylene resin; molybdenum disulfide powders; silicone resin powders; silicone rubber powders; and silica. These lubricants may be used alone or in combination of two or more. Among these lubricants, stearic acid, zinc stearate, and calcium stearate are preferred from the viewpoint of the required low resin surface frictionality of various seal products, and excellent processability.

[0162]

<Inorganic filler (F)>

Examples of materials usable as the inorganic filler (F) in the present invention include, but are not limited to, titanium oxide, zinc sulfide, zinc oxide, carbon black, calcium carbonate, calcium silicate, clay, kaoline, silica, mica powder, alumina, glass fibers, metal fibers, potassium titanate whiskers, asbestos, wollastonite, mica, talc, glass flakes, milled fibers, and metal powders. These materials may be used alone or in combination of two or more. Among these materials, carbon black and titanium oxide are preferred from the viewpoint of the required high elastic modulus and weather resistance of various seal products, and usability as pigments.

[0163]

<Process for producing composition>

A seal product of the present invention is produced using the acrylic block copolymer (A) or a composition of the acrylic block copolymer (A) with at least one of the crosslinked and (or) uncrosslinked rubber (B), the thermoplastic resin and (or) the thermoplastic elastomer (D), and the lubricant (E) and (or) the inorganic filler (F).

[0164]

As a nonlimiting example of a method for processing or producing the composition, an existing method comprising mechanically mixing with, for example, a Banbury mixer, a roller mill, a kneader, a single-screw or multi-screw extruder, or the like, and then pelletizing the resultant mixture can be used.

[0165]

The melt-kneading temperature may be controlled according to the melting temperatures of the used components, such as the acrylic block copolymer (A), the crosslinked and (or) uncrosslinked rubber (B), the thermoplastic resin (C) and (or) the thermoplastic elastomer (D), and the lubricant (E) and (or) the inorganic filler (F). For example, the melt-kneading temperature for production is 130°C to 300°C.

[0166]

According to the required characteristics of various seal products, a stabilizer (an age resister, a

photostabilizer, an ultraviolet absorber, or the like), a flexibilizer, a flame retardant, a mold release agent, an antistatic agent, an antibacterial-antifungal agent, and the like may be added to the acrylic block copolymer (A) or the composition of the acrylic block copolymer (A) with at least one of the crosslinked and (or) uncrosslinked rubber (B), the thermoplastic resin (C) and (or) the thermoplastic elastomer (D), and the lubricant (E) and (or) the inorganic filler (F), which are used for producing the seal products of the present invention. As the additives, optimum additives may be appropriately selected according to the required physical properties of various seal products and workability.

[0167]

Examples of the stabilizer (an age resister, a photostabilizer, an ultraviolet absorber, or the like) include the compounds below, but the stabilizer is not limited thereto.

[0168]

Examples of the age resister include amine age resisters, such as phenyl- $\alpha$ -naphthylamine (PAN), octyldiphenylamine, N,N'-diphenyl-p-phenylenediamine (DPPD), N,N'-di- $\beta$ -naphthyl-p-phenylenediamine (DNPD), N-(1,3-dimethyl-butyl)-N'-phenyl-p-phenylenediamine, N-phenyl-N'-isopropyl-p-phenylenediamine (IPPN), N,N'-diallyl-p-

phenylenediamine, phenothiazine derivatives, diallyl-p-phenylenediamine mixtures, alkylated phenylenediamines, 4,4'- $\alpha,\alpha$ -dimethylbenzyldiphenylamine, p,p-toluenesulfonylaminodiphenylamine, N-phenyl-N'-(3-methacryloyloxy-2-hydropropyl)-p-phenylenediamine, diallylphenylenediamine mixtures, diallyl-p-phenylenediamine mixtures, N-(1-methylheptyl)-N-phenyl-p-phenylenediamine, and diphenylamine derivatives; imidazole age resistors, such as 2-mercaptopbenzoimidazole (MBI); phenyl age resistors, such as 2,6-di-tert-butyl-4-methylphenol; phosphate age resistors, such as nickel diethyl-dithiocarbamate; and secondary age resistors, such as triphenylphosphite.

Examples of the photostabilizer and the ultraviolet absorber include 4-tert-butylphenylsalicylate, 2,4-dihydroxybenzophenone, 2,2'-dihydroxy-4-methoxybenzophenone, ethyl-2-cyano-3,3'-diphenylacrylate, 2-ethylhexyl-2-cyano-3,3'-diphenylacrylate, 2-hydroxy-5-chlorobenzophenone, 2-hydroxy-4-methoxybenzophenone-2-hydroxy-4-octoxybenzophenone, monoglycol salicylate, oxalic amide, and 2,2',4,4'-tetrahydrobenzophenone. These compounds may be used alone or in combination of two or more.

[0169]

Examples of the flexibilizer include plasticizers ordinarily added to thermoplastic resins and rubber, softeners, oligomers, oils (animal oil and vegetable oil),

and petroleum fractions (kerosene, light oil, heavy oil, and naphtha).

[0170]

Examples of the softeners include process oils, for example, petroleum process oils, such as paraffin oil, naphthenic process oil, and aromatic process oil.

[0171]

Examples of the plasticizers include phthalic acid derivatives, such as dimethyl phthalate, diethyl phthalate, di-n-butyl phthalate, di-(2-ethylhexyl) phthalate, diheptyl phthalate, diisodecyl phthalate, di-n-octyl phthalate, diisononyl phthalate, ditridecyl phthalate, octyldecyl phthalate, butylbenzyl phthalate, and dicyclohexyl phthalate; isophthalic acid derivatives, such as dimethyl isophthalate; tetrahydronphthalic acid derivatives, such as di-(2-ethylhexyl)tetrahydronphthalic acid; adipic acid derivatives, such as dimethyl adipate, dibutyl adipate, di-n-hexyl adipate, di-(2-ethylhexyl) adipate, dioctyl adipate, isononyl adipate, diisodecyl adipate, and dibutyl diglycol adipate; azelaic acid derivatives, such as di-2-ethylhexyl azelate; sebacic acid derivatives, such as dibutyl sebacate; dodecan-2-oic acid derivatives; maleic acid derivatives such as dibutyl maleate and di-2-ethylhexyl maleate; fumaric acid derivatives, such as dibutyl fumarate; p-oxybenzoic acid derivatives, such as 2-ethylhexyl p-oxybenzoate; trimellitic

acid derivatives, such as tris-2-ethylhexyl trimellitate; pyromellitic acid derivatives; citric acid derivatives, such as acetyl tributyl citrate; itaconic acid derivatives; oleic acid derivatives; ricinoleic acid derivatives; stearic acid derivatives; other fatty acid derivatives; sulfonic acid derivatives; phosphoric acid derivatives; glutaric acid derivatives; polyester plasticizers comprising a polymer of a dibasic acid, such as adipic acid, azelaic acid, phthalic acid, or the like, and glycol or a monohydric alcohol; glycol derivatives; glycerin derivatives; paraffin derivatives, such as chlorinated paraffin; epoxy derivatives; polyester polymer plasticizers; polyether polymer plasticizers; carbonate derivatives, such as ethylene carbonate and propylene carbonate; benzenesulfonic acid derivatives, such as N-butylbenzenamide. In the present invention, the plasticizer is not limited to these plasticizers, and various plasticizers, such as commercially available plasticizers for rubber or thermoplastic resins, can be used.

[0172]

Examples of the commercially available plasticizers include Thiokol TP (produced by Morton Corporation), Adekacizer O-130P, C-79, UL-100, P-200, and RS-735 (produced by Asahi Denka Co., Ltd.), Sansocizer N-400 (produced by Shin-Nippon Rika Co., Ltd.), BM-4 (produced by Daihachi

Chemical Industry Ltd.), EHPB (produced by Ueno Fine Chemicals Industry, Ltd.), and UP-1000 (produced by Toagosei Co., Ltd.).

[0173]

Examples of the oils include vegetable oils, such as castor oil, cottonseed oil, linseed oil, rapeseed oil, soybean oil, palm oil, coconut oil, peanut oil, pine oil, tall oil, sesame oil, and camellia oil.

[0174]

Other examples of the flexibilizer include polybutenic oil, spindle oil, machine oil, and tricresylphosphate.

[0175]

The flexibilizer used preferably has excellent affinity for the acrylic block copolymer (A), the thermoplastic resin (C), and the thermoplastic elastomer (D). Preferred examples of such a flexibilizer include low-volatile plasticizers causing small heating losses, such as adipic acid derivatives, phthalic acid derivatives, glutaric acid derivatives, trimellitic acid derivatives, pyromellitic acid derivatives, polyester plasticizers, glycerin derivatives, epoxy derivatives; polyester polymer plasticizers, and polyether polymer plasticizers.

[0176]

Examples of the flame retardant include, but are not limited to, compounds such as triphenyl phosphate, tricresyl

phosphate, decabromobiphenyl, decabromobiphenyl ether, and antimony trioxide. These compounds may be used alone or in combination of two or more.

[0177]

In order to improve compatibility of the acrylic block copolymer (A) with the crosslinked and (or) uncrosslinked rubber (B), the thermoplastic resin (C) and (or) the thermoplastic elastomer (D), any of various graft polymers and block polymers may be used as the compatibilizer.

[0178]

Commercially available products of the compatibilizer include Kraton Series (produced by Shell Japan Co.,), Toughtec Series (produced by Asahi Chemical Industry Co.,), Dynaron (produced by Nippon Synthetic Rubber K.K.), Eblend (produced by Daicel Chemical Industries Ltd.), Septon (produced by Kuraray Co., Ltd.), Nofalloy (produced by NOF Corporation), Rexpearl (Nippon Petrochemical Co., Ltd.), Bondfast (produced by Sumitomo Chemical Co., Ltd.), Bondine (Sumitomo Chemical Co., Ltd.), Admer (Mitsui Chemicals, Inc.), Youmex (Produced by Sanyo Chemical Industries, Ltd.), VMX (produced by Mitsubishi Chemical Corporation), Modiper (produced by NOF Corporation), Staphyloid (Takeda Chemical Industries, Ltd.), and Reseda (Toagosei Co., Ltd.). The compatibilizer may be appropriately selected and used according to combination with the crosslinked and (or)

uncrosslinked rubber (B), the thermoplastic resin (C) and (or) the thermoplastic elastomer (D) which are used for compensating the physical properties of the block copolymer (A) for seal products.

[0179]

When a composition including the acrylic block copolymer (A), the crosslinked and (or) uncrosslinked rubber (B), the thermoplastic resin (C) and (or) the thermoplastic elastomer (D) is crosslinked (dynamically crosslinked) by dynamic heat-treatment, the type of the crosslinking agent used and the dynamic crosslinking conditions (temperature and time) are not particularly limited and may be appropriately determined according to the type of the acrylic block copolymer (A).

[0180]

As the crosslinking agent, a general rubber crosslinking agent (crosslinking agent) can be used.

[0181]

Examples of the general rubber crosslinking agent include sulfur crosslinking agents, such as powdered sulfur, precipitated sulfur, high-dispersion sulfur, surface-treated sulfur, insoluble sulfur, dimorpholine disulfide, and alkylphenol disulfide; and organic peroxide crosslinking agents, such as benzoyl peroxide, tert-butyl hydroperoxide, 2,4-dichlorobenzoyl peroxide, 2,5-dimethyl-1,5-di(tert-

butylperoxy)hexane, and 2,5-dimethylhexane-2,5-di(peroxybenzoate).

[0182]

When the organic peroxide crosslinking agent is used, a crosslinking auxiliary may be used according to demand.

Examples of the crosslinking auxiliary include polyfunctional vinyl monomers, such as divinylbenzene and triallyl cyanurate; and polyfunctional methacrylate monomers, such as ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, trimethylolpropane trimethacrylate, and allyl methacrylate. The use of such a compound permits uniform and efficient crosslinking reaction.

[0183]

As the crosslinking agent, a mixed crosslinking-type phenol resin crosslinking agent containing a halogen donor, such as a bromide of an alkylphenol resin, tin chloride, or chloroprene, and an alkylphenol resin, or an organosiloxane compound having two or more SiH groups in its molecule can also be used.

[0184]

A crosslinking method using the organosiloxane compound uses selective addition reaction (hydrosilylation reaction) of SiH groups to unsaturated hydrocarbon groups in a rubber component. In order to cause the compound to function as

the crosslinking agent, it is necessary to add the SiH groups to two or more molecules of rubber. Therefore, the crosslinking agent must contain two or more SiH groups in its molecule. As the organosiloxane compound having two or more SiH groups in its molecule, a cyclic polysiloxane, a linear polysiloxane, a compound having the structure of a tetrahedral siloxane, or compounds and (or) polymers derived from these compounds may be used.

[0185]

When the organosiloxane compound having two or more SiH groups in its molecule is used as the crosslinking agent, a group transition metal such as palladium, rhodium, or platinum, or a compound thereof, a complex, a peroxide, an amine, a hydrosilylation catalyst such as phosphine, a system including an organic peroxide and a bismaleimide compound serving as a co-catalyst may be used as a catalyst for promoting hydrosilylation reaction.

[0186]

Other examples of the crosslinking agent include zinc white, magnesium oxide, litharge, p-quinone dioxime, p-dibenzoylquinone dioxime, tetrachloro-p-benzoquinone, poly-p-dinitrosobenzene, and methylenedianiline.

[0187]

If required, a crosslinking promoter and a crosslinking promotion auxiliary may be added.

[0188]

As the crosslinking promoter, a general crosslinking promoter, such as an aldehyde-ammonia type, guanidine type, thiazole type, sulfenamide type, thiuram type, dithionate type, or thiourea type crosslinking promoter can be used.

[0189]

Examples of the aldehyde-ammonia type crosslinking promoter include hexamethylenetetramine; examples of the guanidine type crosslinking promoter include diphenylguanidine; examples of the thiazole type crosslinking promoter include dibenzothiazyl disulfide (DM), 2-mercaptopbenzothiazole and its Zn salt, and cyclohexylamine salt 2-(4'-morpholinodithio)benzothiazole; examples of the sulfonamide-type crosslinking promoter include cyclohexylbenzothiazolyl sulfenamide CBS, N-oxydiethylenebenzothiazolyl-2-sulfenamide, N-tert-butyl-2-benzothiazolylsulfenamide, and 2-(4-morphlinyldithio)benzothiazole; examples of the thiuram-type crosslinking promoter include tetramethylthiuram disulfide (TMTD), tetraethylthiuram disulfide, tetramethylthiuram monosulfide (TMMT), and dipentamethylenethiuram tetrasulfide; examples of the dithionate-type crosslinking promoter include Zn-dimethyldithiocarbamate, Zn-diethyldithiocarbamate, Zn-di-n-butylidithiocarbamate, Zn-ethylphenyldithiocarbamate, Te-diethyldithiocarbamate, Cu-

dimethyldithiocarbamate, Fe-dimethyldithiocarbamate, and pipecolinepipecolyldithiocarbamate; and examples of the thiourea-type crosslinking promoter include ethylenethiourea and diethylthiourea.

[0190]

Examples of the crosslinking promotion auxiliary include general rubber auxiliaries, such as zinc white, stearic acid and oleic acid and Zn salts thereof. The crosslinking promotion auxiliary can be combined with the crosslinking promoter.

[0191]

In the present invention, the necessary crosslinking agent may be appropriately selected according to the dynamic crosslinking conditions (temperature and time), and the physical properties of a composition to be prepared. When a composition to be prepared is required to have heat resistance, the organic peroxide crosslinking agent is preferably used.

[0192]

As a kneading machine used for preparing the composition, any of various apparatuses capable of heating and kneading at the same time, for example, an apparatus ordinarily used for rubber, such as a Banbury mixer, a roll mill, a kneader, or a single-screw or multi-screw (e.g., double-screw) extruder, can be used. The composition is

mechanically mixed with such an apparatus and then palletized by an existing method.

[0193]

The kneading temperature for preparing the composition may be controlled according to the melting temperature of the acrylic block copolymer (A) used. For example, the kneading temperature is preferably 100°C to 300°C and more preferably 150°C to 250°C.

[0194]

The seal products of the present invention can be formed by any desired molding method such as extrusion molding, compression molding, blow molding, calender molding, vacuum molding, foam molding, injection molding, injection blowing, or the like using the composition. Among these methods, injection molding is preferred from the viewpoint of simplicity.

[0195]

The molding conditions for forming the seal products of the present invention using the composition by, for example, injection molding generally include a cylinder temperature of 150°C to 240°C, a nozzle temperature of 200°C, a low injection rate, and a mold temperature of 40°C to 70°C.

[0196]

The seal products of the present invention which are produced by the above-described method have excellent oil

resistance, heat resistance, weather resistance, and compression set and can be preferably used for dust covers and the like. Also, the seal products exhibits simplicity of the molding process and excellent recycle property, as compared with conventional seal products, for example, vulcanized rubber products, and has more excellent oil resistance and weather resistance, as compared with olefinic thermoplastic elastomers.

[0197]

Examples of the seal products include seal products for automobiles, seal products for home electric appliances, and seal products for office appliances. Specific examples of such products include various types of oil seals, such as an oil seal and a reciprocation oil seal; various types of packings, such as a ground packing, a lip packing, and a squeeze packing; various types of dust covers, such as a suspension dust cover, a suspension tie-rod dust cover, and a stabilizer tie-rod dust cover; various types of gaskets, such as a resin intake manifold gasket, a throttle-body gasket, a power-steering vane pump gasket, a head-cover gasket, a water heater self-priming pump gasket, a filter gasket, a pipe joint (ABS & HBB) gasket, a HDD top-cover gasket, a HDD connector gasket, a cylinder-head gasket combined with a metal, a car cooler compressor gasket, a gasket around an engine, an AT separate plate, and general-

purpose gaskets (industrial sewing machine, nailing machine, and the like); various types of valves, such as a needle valve, a plunger valve, a water/gas valve, a brake valve, a drinking valve, and a safety valve for an aluminum electrolytic capacitor; various types of stopper mainly having a buffer function, such as a diaphragm for a vacuum booster or water and gas, a seal washer, a bore plug, and a high-precision stopper; and precision seal rubbers, such as a plug tube seal, an injection pipe seal, an oil receiver, a brake drum seal, a shading seal, a plug seal, a connector seal, and a keyless entry cover. Other examples of seal products include various types of weatherstrips, such as a weatherstrip for automobile parts; a trunk seal, and a glass run channel.

[0198]

[Examples]

Although the seal products of the present invention will be described in detail below on the basis of examples, the present invention is not limited to these examples.

[0199]

In the examples, EA, BA, MEA, MMA, TBMA, TBA, and HEA represent ethyl acrylate, butyl acrylate, 2-methoxyethyl acrylate, methyl methacrylate, tert-butyl methacrylate, tert-butyl acrylate, and 2-hydroxyethyl acrylate, respectively.

[0200]

In the specification, a molecular weight was determined in terms of polystyrene by GPC measurement using a GPC analyzer, chloroform as a mobile phase, and a polystyrene gel column.

[0201]

<Test method>

(Molecular weight)

The molecular weight of an acrylic block copolymer was determined using a GPC analyzer (system: GPC system produced by Waters Corporation, column: Shodex K-804 (polystyrene gel) produced by Show Denko K.K.) and chloroform as the mobile phase. The molecular weight was determined in terms of polystyrene.

[0202]

(Analysis of conversion to six-membered ring acid anhydride group)

Reaction of conversion to a six-membered ring acid anhydride group in an acrylic block copolymer was confirmed by infrared spectrum analysis (using FTIR-8100 produced by Shimadzu Corporation) and nuclear magnetic resonance analysis (using AM400 produced by BRUKER Corporation).

[0203]

As a measurement solvent for nuclear magnetic resonance analysis, deuteriochloroform was used for both a block having

a carboxylic ester and a block having a six-membered ring acid anhydride structure.

[0204]

(Analysis of conversion to acid group)

Reaction of decomposition to a carboxylic acid group-containing unit in an acrylic block copolymer was confirmed by an infrared spectrum analysis (using FTIR-8100 produced by Shimadzu Corporation) and nuclear magnetic resonance analysis (using AM400 produced by BRUKER Corporation).

[0205]

As a measurement solvent for nuclear magnetic resonance analysis, deuterochloroform was used for a block having a carboxylic ester, and deuteroacetone was used for a block containing a carboxylic acid.

[0206]

(Hardness)

Hardness at 23°C (JIS A) was measured according to JIS K6301.

[0207]

(Tensile properties (mechanical strength))

According to the method of JIS K7113, mechanical strength was measured by AG-10TB model autograph produced by Shimadzu Corporation. Measurement was performed with n = 3, and averages of strength (MPa) and elongation (%) at breakage of a specimen were used. The specimen had a shape

of No. 2(1/3) having a thickness of about 2 mm. A test was carried out at 23°C and a test rate of 500 mm/min. As a rule, the specimen was conditioned at a temperature of 23±2°C and relative humidity of 50±5% for 48 hours or more before the test.

[0208]

(Compression set)

According to JIS K6301, a cylindrical molded product was maintained with a compression rate of 25% at 70°C, 100°C, 120°C, or 150°C for 22 hours or 72 hours, and then allowed to stand at room temperature for 30 minutes. Then, the thickness of the molded product was measured to calculate residual strain.

[0209]

Namely, a compression set of 0% corresponds to complete recovery of strain, and a compression set of 100% corresponds to no recovery of strain.

[0210]

(Oil resistance)

According to ASTM D638, a molded product of a composition was maintained in ASTM No. 3 oil kept at 150°C for 72 hours to determine a rate of weight change (% by weight). Also, the shape after immersion in oil was evaluated based on the following criteria:

Shape: maintained = O, slightly swollen = O ~ Δ,

swollen = Δ, significantly swollen or partially dissolved = ×, completely dissolved = ××

[0211]

(Frictionality)

In order to measure frictionality due to friction between samples of the same material according to JIS K7215, a dynamic coefficient of friction was determined by SURFACE PROPERTY TESTER (produced HEIDON Corporation, TYPE: 14DR) using a test piece having a shape of 80 × 200 mm and a counter piece having a shape of 20 × 20 mm, both pieces being cut out of a sheet having a thickness of 2 mm. A test was performed at a load of 100 gf and a rate of 50 mm/min. When frictionality could not be measured because of high tackiness, frictionality was evaluated as ×.

[0212]

(Recycling property)

A sheet formed for evaluating the tensile properties and the like was again milled and kneaded by Labo Plastomill (produced by Toyo Seiki Co., Ltd.) at a temperature of processing for producing the sheet, and then pressed at each of temperatures.

[0213]

When the sheet similar to that before kneading was obtained, the recycling property was evaluated as good (O). When the sheet similar to that before kneading was not be

obtained, the recycling property was evaluated as bad (x).

[0214]

(Low-temperature brittleness)

According to JIS K7216, a sample of 38 × 6 mm was cut out from a molded sheet of 2 mm in thickness, and the low-temperature brittle temperature was measured by a low-temperature brittle temperature measuring device (Toyo Seiki Co., Ltd.).

[0215]

(Processability)

A molded sheet of 2 mm in thickness produced for evaluating the tensile properties and the like was cut into pellets, and the processing temperature was measured with melt viscosity (1500 poise) by Capilograph (produced by Toyo Seiki Co., Ltd.).

Conditions: capillary length, 10 mm; capillary diameter, 1 mm; barrel diameter 9.55 mm

[0216]

<Production of acrylic block copolymer>

Production Example 1 [Synthesis of (MMA-co-TBMA)-b-(BA-co-EA-co-MEA)-b-(MMA-co-TBMA) (MMA/TBMA = 80/20 (mol%), (BA-co-EA-co-MEA) / (MMA-co-TBMA) = 60/40 (% by weight)) block copolymer (referred to as "20T3A6" hereinafter)]

The procedures below were preformed for producing 20T3A6.

[0217]

The air in a 5L separable flask used as a polymerization vessel was replaced by nitrogen, and 10.6 g (73.7 mmol) of copper bromide and 140 ml of acetonitrile (bubbled with nitrogen) were added to the flask. After stirring under heating at 70°C for 30 minutes, 5.31 g (14.8 mmol) of diethyl 2,5-dibromoadipate serving as an initiator, 281 ml (1.96 mol) of BA, 267 ml (2.47 mol) of EA, and 151 ml (1.18 mol) of MEA were added to the flask. The resultant mixture was stirred under heating at 85°C, and 1.54 ml (7.38 mmol) of diethylenetriamine was added as a ligand to initiate polymerization.

[0218]

After the initiation of polymerization, 0.2 ml of a solution was sampled from the polymerization solution with predetermined time intervals, and the BA conversion rate was determined by gas chromatographic analysis of each sampled solution. The polymerization rate was controlled by adding diethylenetriamine at any desired time. At a BA conversion rate of 94%, an EA conversion rate of 94%, and an MEA conversion rate of 96%, 129 ml (0.8 mol) of TBMA, 341 ml (3.19 mol) of MMA, 7.30 g (73.8 mmol) of copper chloride, 14 ml (0.1 mol) of butyl acetate, and 1739 ml of toluene (bubbled with nitrogen) were added to the reaction solution. Similarly, the conversion rates of TBMA and MMA were

determined. At a TBMA conversion rate of 61% and an MMA conversion rate of 56%, 1500 ml of toluene was added to the reaction solution, and the reactor was cooled in a water bath to terminate the reaction.

[0219]

The reaction solution was diluted with 2.0 L of toluene, and then 17.9 g of p-toluenesulfonic acid monohydrate was added to the reaction solution, followed by stirring at room temperature for 3 hours. Then, 12.0 g of Kyowaad 500SH (produced by Kyowa Chemical Industry Co., Ltd.) was added as an adsorbent to the polymer solution, followed by further stirring at room temperature for 3 hours. Then, the adsorbent was filtered off with a Kiriyama funnel to produce a colorless transparent polymer solution. The resultant solution was dried to remove the solvent and the residual monomers, and thereby the target acrylic block copolymer 20T3A6 was obtained.

[0220]

GPC analysis of the resultant acrylic block copolymer 20T3A6 showed a number-average molecular weight ( $M_n$ ) of 118,927 and a molecular weight distribution ( $M_w/M_n$ ) of 1.49.

[0221]

Production Example 2 [Synthesis of (MMA-co-TBMA) -b- (BA-co-EA-co-MEA) -b- (MMA-co-TBMA) (MMA/TBMA = 50/50 (mol%), (BA-co-EA-co-MEA) / (MMA-co-TBMA) = 60/40 (% by weight)) block

copolymer (referred to as "50T3A6" hereinafter)]

The target acrylic block copolymer (50T3A6) was produced by the same method as in Production Example 1 except the following procedures: In a 5L separable flask, 5.31 g (14.8 mmol) of diethyl 2,5-dibromoadipate, 281 ml (1.96 mol) of BA, 267 ml (2.47 mol) of EA, and 151 ml (1.18 mol) of MEA were charged and subjected to polymerization. At a BA conversion rate of 95%, an EA conversion rate of 95%, and an MEA conversion rate of 98%, 435 ml (2.70 mol) of TBMA and 287 ml (2.70 mol) of MMA were added to the reaction solution. At a TBMA conversion rate of 67% and an MMA conversion rate of 59%, the reaction was terminated.

[0222]

GPC analysis of the resultant acrylic block copolymer (50T3A6) showed a number-average molecular weight ( $M_n$ ) of 96,778 and a molecular weight distribution ( $M_w/M_n$ ) of 1.46.

[0223]

Production Example 3 [Synthesis of TBMA-b-(BA-co-EA-co-MEA)-b-TBMA ((BA-co-EA-co-MEA)/TBMA = 60/40 (% by weight)) block copolymer (referred to as "100T3A6" hereinafter)]

The target acrylic block copolymer (100T3A6) was produced by the same method as in Production Example 1 except the following procedures: In a 5L separable flask, 5.69 g (15.8 mmol) of diethyl 2,5-dibromoadipate, 301 ml (2.10 mol) of BA, 286 ml (2.64 mol) of EA, and 162 ml (1.26

mol) of MEA were charged and subjected to polymerization. At a BA conversion rate of 96%, an EA conversion rate of 96%, and an MEA conversion rate of 98%, 636 ml (3.94 mol) of TBMA was added to the reaction solution. At a TBMA conversion rate of 77%, the reaction was terminated.

[0224]

GPC analysis of the resultant acrylic block copolymer (100T3A6) showed a number-average molecular weight ( $M_n$ ) of 90,416 and a molecular weight distribution ( $M_w/M_n$ ) of 1.43.

[0225]

Production Example 4 [Synthesis of TBMA-b-(BA-co-MEA)-b-TBMA ((BA-co-MEA)/TBMA = 60/40 (% by weight)) block copolymer (referred to as "100T2A6" hereinafter)]

The target block copolymer (100T2A6) was produced by the same method as in Production Example 1 except the following procedures: In a 5L separable flask, 5.45 g (15.1 mmol) of diethyl 2,5-dibromoadipate, 369 ml (2.57 mol) of BA, and 331 ml (2.57 mol) of MEA were charged and subjected to polymerization. At a BA conversion rate of 94% and an MEA conversion rate of 97%, 503 ml (3.10 mol) of TBMA was added to the reaction solution. At a TBMA conversion rate of 72%, the reaction was terminated.

[0226]

GPC analysis of the resultant block copolymer (100T2A6) showed a number-average molecular weight ( $M_n$ ) of 80,400 and

a molecular weight distribution ( $M_w/M_n$ ) of 1.55.

[0227]

Production Example 5 [Synthesis of MMA-(BA-co-HEA)-MMA block copolymer (referred to as "10HBA7" hereinafter)

The procedures below were performed for producing 10HBA7.

[0228]

The target block copolymer (10HBA7) was produced by the same method as in Production Example 1 except the following procedures: In a 500ml separable flask, 5.8 g (16.3 mmol) of diethyl 2,5-dibromoadipate serving as an initiator, 832 ml (5.8 mol) of BA, and 67.5 ml (0.6 mol) of HEA were charged and subjected to polymerization. At a BA conversion rate of 95% and a HEA conversion rate of 100%, 374 ml (3.5 mol) of MMA was added to the reaction solution. At an MMA conversion rate of 61%, the reaction was terminated.

[0229]

GPC analysis of the resultant block copolymer showed a number-average molecular weight ( $M_n$ ) of 130,010 and a molecular weight distribution ( $M_w/M_n$ ) of 1.67. Also,  $^1\text{H-NMR}$  analysis of the composition showed that BA/HEA/MMA = 65/7/28 (% by weight).

[0230]

Production Example 6 [Synthesis of (MMA-co-TBMA)-b-BA-b-(MMA-co-TBMA) (MMA/TBMA = 80/20 (mol%), BA/(MMA-co-TBMA) =

70/30 (% by weight)) block copolymer (referred to as "20TBA7" hereinafter)]

The target acrylic block copolymer (20TBA7) was produced by the same method as in Production Example 1 except the following procedures: In a 5L separable flask, 5.65 g (15.7 mmol) of diethyl 2,5-dibromoadipate and 900 ml (6.28 mol) of BA were charged and subjected to polymerization. At a BA conversion rate of 95%, 151.9 ml (0.94 mol) of TBMA and 400.9 ml (3.77 mol) of MMA were added to the reaction solution. At a TBMA conversion rate of 70% and an MMA conversion rate of 64%, the reaction was terminated.

[0231]

GPC analysis of the resultant block copolymer (20TBA7) showed a number-average molecular weight ( $M_n$ ) of 122,858 and a molecular weight distribution ( $M_w/M_n$ ) of 1.46.

[0232]

In addition, 700 g of the block copolymer (20TBA7) produced in Production Example 6 and 1.4 g of Irganox 1010 (produced by Ciba-Geigy Corporation) were melt-kneaded at 70 rpm for 20 minutes with a pressure kneader (DS1-5MHB-E model kneader, produced by Moriyama Co., Ltd.) set at 240°C to produce the target six-membered ring acid anhydride group-containing block copolymer (referred to as "20ANBA7" hereinafter). Furthermore, 600 g of the resultant six-

membered ring acid anhydride group-containing block copolymer (20ANBA7) was placed in a pressure-resistant vessel together with 2500 g of water, and the resulting mixture was heated at 200°C for 2 hours to obtain the target carboxyl group-containing block copolymer (referred to as "20CBA7" hereinafter).

[0233]

Production Example 7 [Synthesis of MMA-BA-MMA (BA/MMA = 70/30 (% by weight)) block copolymer (referred to as "MBAM" hereinafter)]

The procedures below were performed for producing MBAM.

[0234]

The air in a 5L separable flask was replaced by nitrogen, and 11.3 g (78.5 mmol) of copper bromide and 180 mL of acetonitrile (dried over molecular sieves and then bubbled with nitrogen) were added to the flask. After stirring under heating at 70°C for 5 minutes, the temperature was returned to room temperature, and then 5.7 g (15.7 mmol) of diethyl 2,5-dibromoadipate serving as an initiator and 804.6 g (900.0 ml) of BA were added to the flask. The resultant mixture was stirred under heating at 80°C, and 1.6 ml (7.9 mmol) of diethylenetriamine was added as a ligand to initiate polymerization. After the initiation of polymerization, about 0.2 ml of a solution was sampled from the polymerization solution with predetermined

time intervals, and the conversion rate of BA was determined by gas chromatographic analysis of each sampled solution. The polymerization rate was controlled by adding diethylenetriamine at any desired time. At a BA conversion rate of 95%, 345.7 g (369.3 ml) of MMA, 7.8 g (78.5 mmol) of copper chloride, 1.6 ml (7.9 mmol) of diethylenetriamine, and 1107.9 ml of toluene (dried over molecular sieves and then bubbled with nitrogen) were added to the reaction solution. Similarly, the MMA conversion rate was determined.

[0235]

At an MMA conversion rate of 85% and a BA conversion rate of 98%, 1500 ml of toluene was added to the reaction solution, and the reactor was cooled in a water bath to terminate the reaction.

[0236]

The polymerization solution was constantly green during the reaction.

[0237]

The reaction solution was diluted with 4000 ml of toluene, and then 22.1 g of p-toluenesulfonic acid monohydrate was added to the reaction solution, followed by stirring at room temperature for 3 hours. The insoluble precipitate was filtered off with a Kiriyama funnel, and then 9.7 g of an adsorbent (Kyowaad 500SH) was added to the resultant polymer solution, followed by further stirring at

room temperature for 3 hours. Then, the adsorbent was filtered off with a Kiriyama funnel to produce a colorless transparent polymer solution. The resultant solution was dried to remove the solvent and the residual monomers, and thereby the target MBAM was obtained.

[0238]

GPC analysis of the resultant MBAM showed a number-average molecular weight ( $M_n$ ) of 119,200 and a molecular weight distribution ( $M_w/M_n$ ) of 1.51. Also, NMR analysis of the composition showed that BA/MMA = 72/28 (% by weight).

[0239]

Production Example 8 [Synthesis of MMA-b-(BA-co-EA-co-MEA)-b-MMA ((BA-co-EA-co-MEA)/MMA = 70/30 (% by weight)) block copolymer (referred to as "M3AM" hereinafter)

The procedures below were performed for producing M3AM.

[0240]

In a 500 ml separable flask, 1.37 g (9.5 mmol) of copper bromide, 20 ml of acetonitrile (bubbled with nitrogen), 0.69 g (1.9 mmol) of diethyl 2,5-dibromoadipate serving as an initiator, 40.2 ml (280 mmol) of BA, 38.2 ml (352 mmol) of EA, and 21.6 ml (168 mmol) of MEA were added to the flask by the same procedures as in Example 1. Then, 0.20 ml (1.0 mmol) of diethylenetriamine was added as a ligand to initiate polymerization.

[0241]

At a BA conversion rate of 95%, an EA conversion rate of 95%, and an MEA conversion rate of 96%, 42.8 ml (400 mmol) of MMA, 1.82 g (18.5 mmol) of copper chloride, 0.20 ml (1.0 mmol) of diethylenetriamine, and 128.5 ml of toluene (bubbled with nitrogen) were added to the reaction solution. At a BA conversion rate of 97%, an EA conversion rate of 97%, an MEA conversion rate of 98%, and an MMA conversion rate of 82%, 150 ml of toluene was added to the reaction solution, and the reactor was cooled in a water bath to terminate the reaction.

[0242]

The reaction solution was diluted with 400 ml of toluene, and then 2.21 g of p-toluenesulfonic acid monohydrate was added to the reaction solution, followed by stirring at room temperature for 3 hours. The insoluble precipitate was filtered off with a Kiriyama funnel, and then 0.97 g of an adsorbent (Kyowaad 500SH) was added to the resultant polymer solution, followed by further stirring at room temperature for 3 hours. Then, the adsorbent was filtered off with a Kiriyama funnel to produce a colorless transparent polymer solution. The resultant solution was dried to remove the solvent and the residual monomers, and thereby the target M3AM was obtained.

[0243]

GPC analysis of the resultant block copolymer showed a

number-average molecular weight (Mn) of 113,000 and a molecular weight distribution (Mw/Mn) of 1.49.

[0244]

Also, analysis of the composition showed that EA/BA/MEA/MMA = 24/33/15/28 (% by weight).

[0245]

Example 1 [Reaction of conversion to six-membered ring acid anhydride group in block copolymer 20T3A6 and characteristic evaluation]

First, 700 g of the block copolymer (20T3A6) produced in Production Example 1 and 1.4 g of Irganox 1010 (produced by Ciba-Geigy Corporation) were melt-kneaded at 70 rpm for 20 minutes with a pressure kneader (DS1-5MHB-E model kneader produced by Moriyama Co., Ltd.) set at 240°C to produce the target six-membered ring acid anhydride group-containing block copolymer (referred to as "20AN3A6" hereinafter).

[0246]

Conversion to a six-membered ring acid anhydride group of a tert-butyl ester site could be confirmed by IR (infrared absorption spectrum) analysis and  $^{13}\text{C}$ -NMR (nuclear magnetic resonance spectrum) analysis.

[0247]

Namely, in IR analysis, an absorption spectrum derived from the acid anhydride group was observed at about  $1800\text{ cm}^{-1}$  after conversion. In  $^{13}\text{C}$ -NMR analysis, signals at 82 ppm

derived from methine carbon and 28 ppm derived from methyl carbon of a tert-butyl group, respectively, disappeared after conversion

[0248]

The resultant bulk sample was molded by heat pressing at 240°C to produce a cylindrical molded product of 30 mm in diameter and 12 mm in thickness for evaluating compression set. The molded product was used for measuring hardness and compression set.

[0249]

Similarly, a molded sheet product having a thickness of 2 mm was produced by heat pressing. The molded sheet product was used for measuring oil resistance and tensile properties.

[0250]

Furthermore, the sheet molded product was again milled and kneaded by Labo Plastomill for evaluating the recycling property.

[0251]

The results are shown in Table 1.

[0252]

Examples 2 to 4 [Reaction of conversion to six-membered ring acid anhydride group and characteristic evaluation]

The block copolymers produced in Production Examples 2 to 4 were used for producing six-membered ring acid

anhydride group-containing block copolymers (the resultant block copolymers are referred to as "50AN3A6", "100AN3A6", and "100AN2A6", respectively, hereinafter) according to the same procedures as in Example 1.

[0253]

Also, cylindrical molded products of 30 mm in diameter and 12 mm in thickness for evaluating compression set were formed by the same procedures as in Example 1. These molded products were used for measuring hardness and compression set.

[0254]

Similarly, molded sheet products of 2 mm in thickness were formed by heat pressing. These sheet products were used for measuring oil resistance and tensile properties.

[0255]

The molded sheet products were again milled and kneaded by Plastomill for evaluating the recycling property.

[0256]

The results are shown in Table 1.

[0257]

Examples 5 to 7 [Hydrolytic carboxylation of six-membered ring acid anhydride group-containing block copolymer and characteristic evaluation]

First, 600 g of each of the six-membered ring acid anhydride group-containing block copolymers (20AN3A6,

50AN3A6, and 100AN3A6) produced in Examples 1 to 3 and 2500 g of water were placed in a pressure-resistant vessel, and the resultant mixtures were heated at 200°C for 2 hours to produce the target carboxyl group-containing block copolymers (referred to as "20C3A6", "50C3A6", and "100C3A6" hereinafter).

[0258]

Conversion of the six-member ring acid anhydride group to a carboxyl group could be confirmed by IR analysis and  $^{13}\text{C}$ -NMR analysis. Namely, in IR analysis, an absorption spectrum at about 1800  $\text{cm}^{-1}$  derived from the acid anhydride group disappeared after conversion. In  $^{13}\text{C}$ -NMR analysis, a signal at 172 ppm derived from the acid anhydride group was quantitatively shifted to a signal at 180 to 182 ppm derived from the carboxyl group.

[0259]

Also, 100 parts of each resultant carboxyl group-containing block copolymer was mixed with 0.2 parts of Irganox 1010 (Ciba-Geigy Corporation), and the resultant mixture was melt-kneaded at 100 rpm for 20 minutes with Labo Plastomill (produced by Toyo Seiki Co., Ltd.) set at each of temperatures (20C3A6/180°C, 50C3A6/200°C, and 100C3A6/230°C) to produce a bulk sample.

[0260]

Furthermore, the bulk samples were heat-pressed at

respective temperatures (20C3A6/180°C, 50C3A6/200°C, and 100C3A6/230°C) to obtain cylindrical molded products of 30 mm in diameter and 12 mm in thickness for evaluating compression set. These molded products were used for measuring hardness and compression set.

[0261]

Similarly, molded sheet products of 2 mm in thickness were formed by heat pressing. These sheet products were used for measuring oil resistance and tensile properties.

[0262]

The molded sheet products were again milled and kneaded by Plastomill for evaluating the recycling property.

[0263]

The results are shown in Table 1.

[0264]

Example 8 [Amidation reaction of six-membered ring acid anhydride group-containing block copolymer by adding diethylamine and characteristic evaluation]

First, 20 g of the six-membered ring acid anhydride group-containing block copolymer (50AN3A6) produced in Example 2 and 16 g of diethylamine were placed in a pressure-resistant vessel, and the resultant mixture was heated at 200°C for 4 hours to produce the target amido group-containing block copolymer (referred to as "50N3A6", hereinafter) in a bulk form.

[0265]

Also, the resultant amido group-containing block copolymer was heat-pressed at a temperature of 250°C to obtain a cylindrical molded product of 30 mm in diameter and 12 mm in thickness for evaluating compression set. The molded product was used for measuring hardness and compression set.

[0266]

Similarly, a molded sheet product of 2 mm in thickness was formed by heat pressing. The sheet product was used for measuring oil resistance and tensile properties.

[0267]

The molded sheet product was again milled and kneaded by Plastomill for evaluating the recycling property.

[0268]

The results are shown in Table 1.

[0269]

Comparative Examples 1 and 2

First, 100 parts of each of copolymers produced in Production Examples 7 and 8 was mixed with 0.2 parts of Irganox 1010 (Ciba-Geigy Corporation), and the resultant mixture was melt-kneaded at 50 rpm for 20 minutes with Labo Plastomill (produced by Toyo Seiki Co., Ltd.) set at 190°C to produce a bulk composition.

The resulting compositions were heat-pressed at 190°C

to obtain cylindrical molded products of 30 mm in diameter and 12 mm in thickness for evaluating compression set.

These molded products were used for measuring hardness and compression set.

[0270]

Similarly, molded sheet products of 2 mm in thickness were formed by heat pressing. These sheet products were used for measuring oil resistance and tensile properties.

[0271]

The molded sheet products were again milled and kneaded by Plastomill for evaluating the recycling property.

[0272]

The results are shown in Table 1.

[0273]

Comparative Example 3

Circular samples were cut out from a crosslinked chloroprene molded sheet product having a thickness of 2 mm, and six samples were laminated to obtain a molded product for evaluating compression set. The molded product was used for measuring hardness and compression set.

[0274]

Also, a dumbbell sample and the like cut out from the molded sheet product and used for measuring oil resistance and tensile properties.

[0275]

The molded sheet product was again milled and kneaded by Plastomill for evaluating the recycling property.

[0276]

The results are shown in Table 1.

[0277]

#### Comparative Example 4

Santoprene 211-55 (produced by AES Japan Co., Ltd.), which was an olefinic elastomer, was melt-kneaded with Labo Plastomill (produced by Toyo Seiki Co., Ltd.) set at 170°C at a screw rotational speed of 100 rpm to obtain a sample. The resulting sample was heat-pressed at 170°C to obtain a cylindrical molded product of 30 mm in diameter and 12 mm in thickness. The molded product was used for measuring hardness and compression set.

[0278]

Similarly, a molded sheet product of 2 mm in thickness was formed by heat pressing the sample at 170°C. The sheet product was used for measuring oil resistance and tensile properties.

[0279]

The molded sheet product was again milled and kneaded by Plastomill for evaluating the recycling property.

[0280]

The results are shown in Table 1.

[0281]

### Comparative Example 5

Pelprene P-30B (produced by Toyobo Co., Ltd.), which was an ester elastomer, was melt-kneaded with Labo Plastomill (produced by Toyo Seiki Co., Ltd.) set at 190°C at a screw rotational speed of 50 rpm to obtain a sample.

[0282]

The resulting sample was heat-pressed at 190°C to obtain a cylindrical molded product of 30 mm in diameter and 12 mm in thickness. The molded product was used for measuring hardness and compression set.

[0283]

Similarly, a molded sheet product of 2 mm in thickness was formed by heat pressing the sample at 190°C. The sheet product was used for measuring oil resistance and tensile properties.

[0284]

The molded sheet product was again milled and kneaded by Plastomill for evaluating the recycling property.

[0285]

The results are shown in Table 1.

[Table 1]

Table 1

Example No.	1	2	3	4	5	6	7	8	Comparative Example											
									20AN3	50AN3	100AN3	100AN2	20C3A	50C3	100C3	50N3	MBAM	M3AM	CR	211-55
Block copolymer	A6	A6	A6	A6	6	A6	A6	A6												
Hardness (JIS-A)	45	35	23	29	62	42	30	28												
Tensile properties	Breaking strength (MPa)	11	9	6	5	10	9	5												
	Breaking elongation (%)	295	320	372	255	255	277	325												
Oil resistance	Rate of weight change (wt%)	21.7	19.5	20.6	18.8	16.9	18.4	19.4												
	Shape after immersion	○	○	○	○	○	○	○												
Compression set	70 °C, 22Hr (%)																			
	100 °C, 22Hr (%)	57	39.5																	
	100 °C, 72Hr (%)			57.2																
	120 °C, 72Hr (%)				44.3													33		
Recycling property		○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	

[0287]

Table 1 (Examples 1 to 8 and Comparative Examples 1 to 5) indicates that the block copolymers used in the present invention have the recycling property and excellent compression set and oil resistance and maintains strength necessary for molding. It is also found that cohesive force is improved by introducing a functional group, but the block copolymers are materials exhibiting low hardness, flexibility, and excellent compression set and tensile properties.

[0288]

On the other hand, it is found that the samples of Comparative Examples 1 and 2 have the recycling property, but the sample of Comparative Example 1 has unsatisfactory oil resistance, and the sample of Comparative Example 2 has unsatisfactory compression set. It is also found that the sample of Comparative Example 3 has excellent tensile properties and compression set, but the recycling property is unsatisfactory because it comprises crosslinked rubber. It is further found that the sample of Comparative Example 4 has the recycling property and excellent compression set, but has unsatisfactory oil resistance, and the sample of Comparative Example 5 has the recycling property and satisfactory tensile properties, but has unsatisfactory oil resistance and compression set.

}

[0289]

<Rubber composition and thermoplastic elastomer composition>

Examples 9 and 10

First, 10 parts of rubber 1 (powdery NBR produced by JSR Co., Ltd., PN20HA) and 10 parts of crosslinked rubber 1 (silicone-acryl composite rubber, produced by Mitsubishi Rayon Co., Ltd., S-2001) were added to 100 parts by weight of the carboxyl group-containing block copolymer (20C3A6) in Example 9 and Example 10, respectively. Each of the resultant mixtures was kneaded for 10 minutes with Plastomill set at 180°C at a rotational speed of 100 rpm to obtain a bulk composition. The resultant composition was molded into a cylindrical product of 30 mm in diameter and 12 mm in thickness, and the molded product was used for evaluating hardness and compression set.

[0290]

Also, the composition was heat-pressed at 180°C to obtain a molded product of 2 mm in thickness for evaluating physical properties. The molded product was used for measuring oil resistance and tensile properties.

[0291]

Furthermore, in Example 9, the molded product was used for measuring low-temperature brittleness.

[0292]

The results are shown in Table 2.

[0293]

Example 11

First, 33 parts by weight of rubber 1 (powdery NBR, produced by JSR Co., Ltd., PN20HA) and 33 parts by weight of rubber 2 (silicone rubber produced by Toshiba Silicone Co., Ltd., millable silicone rubber XE20-523-4U) were added to 100 parts by weight of the six-membered ring acid anhydride group-containing block copolymer (100AN3A6). A crosslinking agent 1 (2,5-dimethyl-2,5-ditertiarybutyl peroxyhexane produced by Toshiba Silicone Co., Ltd., TC-8) was gradually added to the resultant mixture during kneading of the mixture with Plastomill set at a temperature of 170°C and a rotational speed of 100 rpm for 10 minutes. Molded products were formed and used for evaluation by the same method as in Example 10 except heat pressing was preformed at a set temperature of 180°C.

[0294]

The results are shown in Table 2.

[0295]

Example 12

Molded products were formed and used for evaluation by the same method as in Example 10 except that 25 parts by weight of a plasticizer 1 (polybutyl acrylate produced by Toa-gosei Co., Ltd., UP-1000), 3 parts by weight of a lubricant 1 (Zn stearate produced by Sakai Chemical Co.,

Ltd., SZ-2000), and 15 parts by weight of an inorganic filler 1 (carbon black, produced by Asahi Carbon Co., Ltd., Asahi #60HN) were added to 100 parts by weight of the carboxyl group-containing block copolymer (20C3A6).

[0296]

The results are shown in Table 2.

[0297]

#### Example 13

Molded products were formed and used for evaluation by the same method as in Example 9 except that 57 parts by weight of crosslinked rubber 1 (silicone-acryl composite rubber, produced by Mitsubishi Rayon Co., Ltd., S-2001) was added 100 parts by weight of the carboxyl group-containing block copolymer (100C3A6), and the resultant mixture was kneaded with Plastomill set at a temperature of 230°C and a rotational speed of 100 rpm for 10 minutes and then heat-pressed at a set temperature of 230°C.

[0298]

The results are shown in Table 2.

[0299]

#### Example 14

Molded products were formed and used for evaluation by the same method as in Example 10 except that 64.5 parts by weight of crosslinked rubber 1 (silicone-acryl composite rubber, produced by Mitsubishi Rayon Co., Ltd., S-2001), 0.6

part of a lubricant 2 (stearic acid, produced by Nacalai Tesque), and 1.6 parts by weight of an inorganic filler 2 (carbon black, produced by Asahi Carbon Co., Ltd., Asahi #15) were added to 100 parts by weight of the carboxyl group-containing block copolymer (100C3A6).

[0300]

The results are shown in Table 2.

[0301]

#### Example 15

Molded products were formed and used for evaluation by the same method as in Example 10 except that 30 parts by weight of a thermoplastic elastomer 1 (Daiamid E47 produced by Ube Industries, Ltd.) was added to 100 parts by weight of the six-membered ring acid anhydride group-containing block copolymer (20ANBA7), and 0.023 part by weight of a crosslinking agent 2 (hexamethylenediamine) was gradually added to the resultant mixture during kneading of the mixture at a set temperature of 190°C and a rotational speed of 100 rpm for 20 minutes, followed by heat pressing at a set temperature of 190°C.

[0302]

The results are shown in Table 2.

[0303]

#### Comparative Example 1A

The molded sheet products of 2 mm in thickness formed

by pressing in Comparative Example 1 was used for evaluating low-temperature brittleness.

[0304]

The results are shown in Table 2.

[0305]

Example 5A

The molded sheet product of 2 mm in thickness formed by pressing in Example 5 was used for evaluating low-temperature brittleness.

[0306]

The results are shown in Table 2.

[0307]

[Table 2]

Table 2

Example No.		9	10	11	12	13	14	15	1A*)	5A
Block copolymer	20G3A6	100	100	100						100
	20DANBA7								100	
	100DAN3A6			100						
	100G3A6					100				
	MBAM									100
	M3AM									
Rubber	Rubber 1	10	33							
	Rubber 2		33							
	Crosslinked rubber 1	10				57	64.5			
Thermoplastic elastomer	Thermoplastic elastomer 1									
	Plasticizer	Plasticizer 1		25						
	Lubricant	Lubricant 1		3						
Lubricant	Lubricant	Lubricant 2					0.6			
	Filler	Inorganic filler 1			15					
		Inorganic filler 2						30		
Crosslinking agent	Crosslinking agent	1		2.5						
		Crosslinking agent 2								
	Hardness (JIS-A)		57	59	30	40	42	46	70	22
Tensile properties	Breaking strength (MPa)	8.3	8.7	2	4	5.3	4.6	5.1	8.6	10
	Breaking elongation (%)	238	200	243	155	230	220	121	339	255
	Rate or weight change (wt%)	15.2	22.1	21	5	40	47	41	54.9	16.9
Oil resistance	Shape after immersion	O	O	O	O	O	O	O	X	O
	Low-temperature brittleness	-25.6	-	-	-	-35.5	-	-	-50	-20.5
	70°C, 22Hz (%)	50.7	49.2	40	62.1	38.1	34.1	44.2	49	49.3
Compression set	100°C, 22Hr (%)									
	150°C, 22Hr (%)									

1A\*) Comparative Example

[0308]

Table 2 (Examples 9 to 15, Comparative Example 1A, and Example 5A) indicates that in Examples 9 to 15, a molded product having desired flexibility, compression set, oil resistance, and tensile properties can be obtained even when rubber or crosslinked rubber is added, a plasticizer is added, or rubber is added and then crosslinked.

[0309]

Comparison of Examples 9 and 13 with Example 5A reveals that by adding NBR rubber or crosslinked rubber containing a silicone rubber component, which has low Tg, the low-temperature brittleness can be improved without deterioration in oil resistance which is characteristic of the present invention.

[0310]

<Filler-containing composition>

Example 16

First, 5 parts by weight of a lubricant 2 (stearic acid, produced by Nacalai Tesque) and 0.25 parts by weight of an inorganic filler 2 (carbon black, produced by Asahi Carbon Co., Ltd., Asahi #15) were added to 100 parts by weight of the carboxyl group-containing block copolymer (20C3A6), and the resultant mixture was kneaded for 10 minutes with Plastomill set at 180°C at a rotational speed of 100 rpm to obtain a bulk composition. The resultant composition was

heat-pressed at 180°C to obtain a cylindrical molded product of 30 mm in diameter and 12 mm in thickness. The molded product was used for evaluating hardness and compression set.

[0311]

Similarly, the composition was heat-pressed to obtain a molded sheet product of 2 mm in thickness. The molded sheet product was used for measuring oil resistance, tensile properties, and frictionality.

[0312]

The workability was also measured.

[0313]

The results are shown in Table 3.

[0314]

#### Example 17

Molded products were formed and used for evaluation by the same method as in Example 16 except that 20 parts by weight of a lubricant 2 (stearic acid, produced by Nacalai Tesque) and 1.25 parts by weight of an inorganic filler 2 (carbon black, produced by Asahi Carbon Co., Ltd., Asahi #15) were added to 100 parts by weight of the six-membered ring acid anhydride group-containing block copolymer (20AN3A6).

[0315]

The results are shown in Table 3.

[0316]

Example 18

Molded products were formed and used for evaluation by the same method as in Example 16 except that 2 parts by weight of a lubricant 4 (zinc stearate, produced by NOF Corporation) and 10 parts by weight of an inorganic filler 1 (carbon black, produced by Asahi Carbon Co., Ltd., Asahi #60HN) were added to 100 parts by weight of the carboxyl group-containing block copolymer (20C3A6).

[0317]

The results are shown in Table 3.

[0318]

Example 19

Molded products were formed and used for evaluation by the same method as in Example 16 except that 5 parts by weight of a lubricant 3 (calcium stearate, produced by Sakai Chemical Co., Ltd., SC-100) and 0.25 parts by weight of an inorganic filler 1 (carbon black, produced by Asahi Carbon Co., Ltd., Asahi #60HN) were added to 100 parts by weight of the carboxyl group-containing block copolymer (20C3A6).

[0319]

The results are shown in Table 3.

[0320]

Comparative Examples 1B and 2A

The molded sheet products of 2 mm in thickness formed by pressing in Comparative Examples 1 and 2 were used for

evaluating frictionality. However, both sheet products had high frictionality and tackiness which could not be measured. The results are shown in Table 3.

[0321]

Example 5B

The molded sheet product of 2 mm in thickness formed by pressing in Example 5 was used for evaluating frictionality. Also, the molded sheet product was finely cut into pellets for measuring the processing temperature.

[0322]

The results are shown in Table 3.

[Table 3]

Table 3

Example No.		16	17	18	19	Comp. 1B	Example 2A	5B
Composition (parts)	20C3A6	100	100	100	100			100
	MBAM					100		
	M3AM					100		
	Lubricant 2	5	20					
	Lubricant 3					5		
	Lubricant 4		2					
	Inorganic filler 1			10	0.25			
	Inorganic filler 2	0.25	1.25					
	Hardness (JIS-A)	71	72	88	69	22	38	62
	Tensile properties	Breaking strength (MPa)	8	8	9	7	8.6	6.6
Oil resistance	Breaking elongation (%)	220	277	157	215	339	621	255
	Rate of weight change (wt%)	11.2	3.7	14.9	12.7	54.9	21	16.9
	Shape after immersion	O	O	O	x	O	O	O
	Dynamic coefficient of friction	7.2	1.5	26	6.2	x	x	x
Frictional	70°C, 22Hr (%)					49	76	
	100°C, 72Hr (%)	53	56	62.5	49			49.3
	120°C, 22Hr (%)							
Processability	Processing temp. (°C) (melt viscosity 1500 poise)	175	-	-	-	-	-	200

[0324]

The results shown in Table 3 (Examples 16 to 19, Comparative Examples 1B and 2A, and Example 5B) indicate that compositions containing the acrylic block copolymer of the present invention, a lubricant, and an inorganic filler exhibit desired flexibility, oil resistance, compression set, and tensile properties, and low dynamic frictionality at resin surfaces.

[0325]

A comparison between Examples 16 and 5B shows that the processing temperature can be decreased by adding a lubricant and an inorganic filler to the acrylic block copolymer of the present invention, and thus satisfactory molding can be performed by injection molding or the like.

[0326]

<Thermoplastic resin composition>

Example 20

First, 100 parts by weight of 10HBA7 produced in Production Example 5, 30 parts by weight of PA (UBESTA 3012U(R), polyamide produced by Ube Industries, Ltd.), and 0.2 part by weight of a stabilizer 2 (Irganox 1010, phenolic stabilizer, produced by Ciba-Geigy Corporation) were melt-kneaded with Labo Plastomill (produced by Toyo Seiki Co., Ltd.) set at 230°C at a rotational speed of 100 rpm. During melt-kneading at a screw rotational speed of 100 rpm and

230°C, 0.0004 part by weight of a catalyst 1 (titanium(IV) tetrabutoxide monomer produced by Wako Pure Chemical Industries, Ltd. trade name) was added to accelerate reaction (dynamic crosslinking). Then, when the torque of the Plastomill become constant and stable, 4 parts by weight of 20CBA7 produced in Production Example 6 was added, followed by melt kneading. Then, 1.84 parts by weight of a stabilizer 1 (PEP-36, phosphorus-based stabilizer produced by Asahi Denka Co., Ltd.) was further added to the mixture to obtain a composition (each number of parts being based on 100 parts by weight of 10HBA7).

[0327]

The resultant composition was heat-pressed at a set temperature of 230°C to obtain a cylindrical molded product of 30 mm in diameter and 2 mm in thickness. The molded product was used for measuring hardness and compression set.

[0328]

Similarly, the composition was heat-pressed at a set temperature of 230°C to obtain a molded sheet product of 2 mm in thickness. The molded sheet product was used for measuring tensile properties and oil resistance.

[0329]

The results are shown in Table 4.

[0330]

Comparative Example 6

According to the same method as in Example 20, 100 parts by weight of 10HBA7 produced in Production Example 5, 30 parts by weight of PA (UBESTA 3012U(R), polyamide produced by Ube Industries, Ltd.), and 0.2 part by weight of a stabilizer 2 (Irganox 1010, phenolic stabilizer, produced by Ciba-Geigy Corporation) were melt-kneaded with Labo Plastomill (produced by Toyo Seiki Co., Ltd.) set at 230°C at a rotational speed of 100 rpm. During melt-kneading at a screw rotational speed of 100 rpm and 230°C, 0.0001 part by weight of a catalyst 1 (titanium(IV) tetrabutoxide monomer) was added to accelerate reaction (dynamic crosslinking). Then, molded products were formed and used for evaluation as in Example 20 except that 1.84 parts by weight of a stabilizer 1 (PEP-36) was further added to the mixture.

[0331]

The results are shown in Table 4.

[0332]

[Table 4]

Table 4

Example No.		20	Comparative Example 6
Composition (parts)	Polymer	10HBA7	100
	Compatibilizer 1	20CBA7	4
	Thermoplastic resin	PA	30
	Catalyst	Catalyst 1	0.0004
	Stabilizer	Stabilizer 1	1.84
		Stabilizer 2	0.2
Evaluation results	Hardness (JIS-A)		86
	Tensile properties (MPa)		21
	Compression set	70°C, 22Hr (%)	54
	Oil resistance	Rate of weight change (wt%)	20
		Shape after immersion	○
			○

[0333]

The results of Table 4 (Example 20 and Comparative Example 6) indicate that in dynamically treating a thermoplastic resin and a hydroxyl group-containing block copolymer, the addition of a carboxyl group-containing block copolymer serving as a compatibilizer improves mechanical strength while maintaining excellent compression set and oil resistance.

[0334]

[Advantages]

The acrylic block copolymers used in the present invention are rich in flexibility and excellent in

mechanical strength, moldability, and oil resistance, and are further rich in reactivity. Therefore, the acrylic block copolymers used in the present invention can be combined with rubber or a thermoplastic resin and/or a thermoplastic elastomer to obtain novel compositions rich in flexibility, oil resistance, and the like. Since the acrylic block copolymers used in the present invention are particularly excellent in oil resistance and compression set, the copolymers can be preferably used for seal products (seal products for automobiles, seal products for home electric appliances, and seal products for office electric appliances).

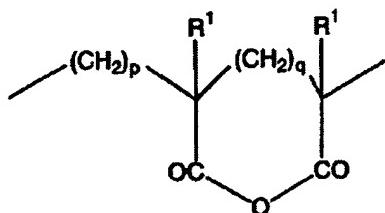
[Name of Document] ABSTRACT

[Abstract]

[Object] To provide seal products, for example, seal products for automobiles, seal products for home electric appliances, and seal products for office electric appliances, which are produced using an acrylic block copolymer rich in flexibility and excellent in oil resistance, moldability, mechanical physical properties, and compression set, and also rich in reactivity.

[Solving Means] A seal product produced by molding an acrylic block copolymer including 10% by weight to 60% by weight of a methacrylic polymer block (a) and 90% by weight to 40% by weight of an acrylic polymer block (b), at least one of the polymer blocks containing, in its main chain, at least one acid anhydride group (c) represented by formula (1) and (or) group derived from the acid anhydride group:

[Chem. 1]



(wherein R¹'s each represent hydrogen or a methyl group and may be the same or different, p represents an integer of 0 or 1, and q represents an integer of 0 to 3).

[Selected Figure]      No